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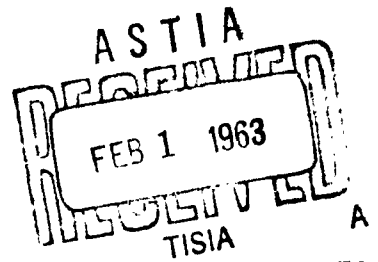ARLINGTON 12, VIRGINIA

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Transport Processes in Fused Salts - Part I

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Technical Progress Report
to the
Office of Naval Research

Contract Nonr-285-37
with New York University

December 1, 1962

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Introduction

Introduction

The study of the transport properties of fused salt systems may be expected to produce information about the structure of fused salts in equilibrium and about the mechanisms of motion. It is of interest per se, for the help it presumably can give in broadening our view of fused salts, for the possibilities it offers of suggesting new approaches to the study of concentrated electrolytic solutions and finally because it offers an opportunity for the critical testing of concepts and theories of transport properties in general.

In this chapter, the hydrodynamic equations of motion of liquid electrolytes will be discussed, identifying each of the transport parameters and the experiments used to study them. The general nature of experimental results will be described and then a detailed discussion of specific results and their implications for particular systems will be presented later. The chapter concludes here with some observations about possible molecular mechanisms of transport.

It must be noted at the outset that the study of transport properties is a variety of kinetics and therefore is subject to certain limitations. Thus, it is necessary to consider the meaning of any experiment in the light of mechanisms postulated for the process. Kinetic studies cannot in any sense prove the correctness of a proposed mechanism. Rather, it is to be expected that some alternative mechanisms can be definitely ruled out and that the compatability of the proposed mechanism with the facts may be demonstrated.

An important difference between classical chemical kinetics

and the study of transport processes lies in the nature of the models.
In our present state of understanding of transport processes in ionic
liquids, no detailed mechanisms of movement have been put forward.
Indeed, we probably do not yet even have a language to describe properly
such motion. The demands made on current theories of transport in
liquid systems to rationalize experimental facts provides one of the
most important reasons for obtaining such experimental results. We
begin with the phenomenological (non-mechanistic) description of
transport properties, which is well advanced, before discussing
molecular mechanisms.

I. Phenomenological Treatment

A. Hydrodynamic Equations

A complete macroscopic description of moving fluid is
embodied in the hydrodynamic equation of motion together with four
accessory equations. The thermal equation of state, $p = p(V,T)$
and the caloric equation of state, $E = E(V,T)$ describe equilibrium
properties. The equation of continuity expresses the conservation
of matter and the equation of energy balance the conservation of energy.
The equation of motion itself is an expression of Newton's Second Law,
$F = d(momentum)/dt$. The solution of the hydrodynamic equation of motion
of a system for particular initial and boundary conditions gives the
velocity of the system at every point and at every instant. The
correct form of this equation must be determined in each given case.
(It is possible to enumerate all the terms which may--but not necessarily
do-- occur in the equation by dimensional analysis).

In the study of the transport properties of liquid electro-
lytes we wish to treat a situation where the experimenter has at his

disposal the parameters pressure, state of shear, external electric field, composition and temperature. The first three are purely mechanical in nature and may readily be described in a force equation. However, the appropriate forces to be associated with composition and thermal gradients must be identified in another way. The methods of non-equilibrium statistical mechanics may be used to relate the forces to microscopic mechanical variables, systematic experimentation might be employed to obtain empirical expressions of the forces, or the so-called"thermodynamics of irreversible processes" might be used to express the forces in terms of gradients of thermodynamic variables.

The development of the set of equations describing the transport behavior of fluids has been discussed by a number of authors, e.g. Leaf (1946), Prigogine (1947, 1952), Kirkwood and Crawford (1952) and Fitts (1962). Assuming that continuous local thermodynamic functions may be defined, the following set of equations may be obtained

$$1/M_i \cdot d\rho_i/dt = -\vec{\nabla} \cdot \vec{J}_i + \sum_k {}_{ik} (d\lambda_k/dt) \tag{1}$$

$$\rho \, d\vec{v}/dt = \vec{X} + \vec{\nabla} \cdot \vec{\vec{\sigma}} \tag{2}$$

$$dS/dt = \Phi/T - \vec{\nabla} \cdot \vec{J}_s \tag{3}$$

where

ρ_i = density of component i, gms cm^{-3}

ρ = density, gms cm^{-3}

t = time

c_i = concentration of species i in formula weight cm^{-3}

M_i = given formula weight of species i

$\vec{V}_i$ = velocity of species i in moles $cm^{-2}sec^{-1}$

$\vec{v}$ = velocity of local center of gravity

$$\sum \rho_i \vec{V}_i = \vec{v} \sum \rho_i = \sum_i \frac{c_i}{M_i} \vec{V}_i / \sum c_i/M_i$$

$\vec{J}_i = c_i(\vec{V}_i - \vec{v})$ = diffusion current density in moles cm^{-2}

γ_{ik} = number of formula weights of i produced in reaction k

λ_k = progress variable of reaction k

$\vec{X}_i$ = external force on a formula weight of species i

$\vec{X}$ = external force density = $\sum c_i \vec{X}_i$ in force cm^{-3}

$\mathcal{T}$ = stress tensor in force cm^{-2}

S = entropy density

ϕ = dissipation function

$\vec{J}_S$ = entropy current density

(Concentrations, forces, etc. per unit mass are often used in order
to simplify some of the equations. Basing quantities on equivalent
weights is apt to be more convenient for chemists.) These express
respectively (1) the change in the amount of species i in a volume
element as the sum of the amount entering (or leaving) and that produced
(or destroyed) by reaction; (2) the net mass times acceleration of the
local center of gravity as the sum of the forces; and (3) the rate of
entropy change as the sum of that produced internally and that lost
(or gained) by flow.

It is then necessary to postulate specific forms for the stress tensor $\vec{\vec{\sigma}}$ and the dissipation function $\vec{\phi}$.

The forces acting on the surface of a given volume element in the fluid are

$$\vec{F} = \int_A \vec{\vec{\sigma}} \cdot \vec{n} \, dA \tag{4}$$

where $\vec{n}$ is the outwardly directed normal at dA and $\vec{\vec{\sigma}}$ is the stress

tensor. For example, the xy component of $\overset{\Rightarrow}{\sigma}$ is the x component of the force exerted on a surface element normal to the y direction. One third of the sum of the diagonal components (the normal stresses) is the negative of the hydrostatic pressure.

$$p = -\frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \tag{5}$$

The off-diagonal terms represent shearing stresses. The total force and the total torque vanish for a volume element moving with uniform velocity in a Galilean frame of reference. From this, it may be shown by a phenomenological argument (e.g. Sommerfeld, 1950) that the stress tensor σ must be symmetric, i.e. $\sigma_{ij} = \sigma_{ji}$. An empirical expression often used (e.g. Fitts, 1962) for the stress tensor of an isotropic fluid is

$$\overset{\Rightarrow}{\sigma} = [2/3 \, (\eta - \varphi) \overset{\Rightarrow}{\nabla} \cdot \overset{\Rightarrow}{v} + p] \, \overset{\Rightarrow}{1} + 2\eta \, \overset{\Rightarrow}{\varepsilon} \tag{6}$$

where

η = coefficient of shear viscosity

φ = coefficient of bulk viscosity

$\overset{\Rightarrow}{\varepsilon}$ = sym $\overset{\Rightarrow}{\nabla}v$, i.e. $\varepsilon_{ij} = 1/2(\partial v_j/\partial x_i + \partial v_i/\partial x_j$

A liquid correctly described by this stress tensor is said to display Newtonian flow. The terms comprising the entropy continuity equation (Eq. 3) may be decomposed as follows:

$$\overset{\Rightarrow}{J}_S = \overset{\Rightarrow}{q}/T + \sum_{i=1}^{N} \overset{\Rightarrow}{J}_i \overset{}{\bar{S}}_i \tag{7}$$

where $\overset{\Rightarrow}{q}$ is the heat flux and $\bar{S}_i$ the partial molal entropy of species i.

The dissipation function ϕ is the sum of a number of quantities dealing in turn with viscous flow, chemical reactions, diffusion and heat flow and is defined to be the rate per unit volume of internal production of entropy. *temperature times*

$$\phi = (\vec{\sigma} + p\vec{I}): \vec{\nabla}\vec{v} - (\Sigma \Delta F_k)d\lambda_k/dt - \sum_{i=1}^{N} \vec{J}_i \cdot \vec{\nabla}_T\tilde{\mu}_i - \vec{q}\cdot\nabla\ln T \qquad (8)$$

$$\vec{\nabla}_T\tilde{\mu}_i = \vec{\nabla}\tilde{\mu}_i + \vec{S}_i\vec{\nabla}\ln T = \vec{\nabla}\mu_i - \vec{F}_i + \vec{S}_i\vec{\nabla}\ln T \qquad (9)$$

That is, $\vec{\nabla}_T\tilde{\mu}_i$ represents the isothermal part of the gradient of the chemical potential including the effect of external forces. For example, if there is an electrical field of local strength $E = -\nabla\psi$, then the force $\vec{F}_i$ on an ion of valence z_i and hence molar charge $z_i\mathcal{F}$ is $z_i\mathcal{F}\nabla\psi$. Thus in this case $\tilde{\mu}_i$ would be the electrochemical potential. Since

$$\sum_i \vec{\nabla}\tilde{\mu}_i \cdot \vec{J}_i = \sum_i \vec{\nabla}\mu_i \cdot \vec{J}_i + \sum_i \vec{\nabla}\psi \cdot \vec{J}_i = \sum_i \vec{\nabla}\mu_i \cdot \vec{J}_i - \vec{E}\cdot\vec{I} \qquad (10)$$

where $\vec{I}$ is the electrical current density; the Joule heat is automatically included in ϕ.

The contribution $-\sum_i(c_i \Delta F_k)d\lambda_k/dt$ represents the effect of chemical reactions. In an electrochemical system a heterogeneous reaction takes place at the interface between the electrodes and electrolyte at a rate given by $A \vec{\nabla}\cdot\vec{I}/nF$, A being the electrode area, $\vec{\nabla}\cdot\vec{I}$ the rate at which current enters a unit volume of electrolyte and n being the number of electrons transferred in the reaction as written. The free energy decrease per Faraday of positive electricity passed from electrode 1 to electrode 2 through the external circuit is

$$-\frac{A}{nF}\vec{\nabla}\cdot\vec{I}\left[\mathcal{E}_0 + \eta_1 - \eta_2 + (\delta v_1)p_1 + (\delta v_2)p_2 + (\delta S_1)T_1 + (\delta S_2)T_2\right] \qquad (11)$$

where $\mathcal{E}_0$ is the equilibrium potential (zero for identical electrodes) η_1, η_2 the respective overpotentials (negative by convention for an anodic process); $\delta v_1, \delta v_2$ the volume changes at the electrodes per Faraday, for the equation as written and $\delta S_1, \delta S_2$ the entropy changes at the electrodes. If homogeneous reactions occur in addition, they may be represented by further terms. For a reversible isothermal iso-baric electrolysis between identical electrodes, the entire expression vanishes.

B The Linear Phenomenological Equations

The dissipation function may be thought of as being a sum of products of two sorts of terms. On the one hand, $\vec{\nabla}\vec{v}_j$, $\vec{J}_i$, $\vec{q}$ and $d\lambda_k/dt$ are fluxes of various quantities and on the other hand $(\vec{\sigma} + p1)$, $\vec{\nabla}_\eta\vec{\mu}_i$, $\rho\Delta F_k$, $\vec{\nabla}\ln T$ are forces. (In this context the term force has only symbolic significance. In general it does not mean Newtonian forces.) Then Φ has the form

$$\Phi = \sum_{i=1}^{N} \vec{J}_i \cdot \vec{X}_i \qquad (12)$$

where $\vec{J}_i$ is a generic symbol for fluxes of various kinds and $\vec{X}_i$ for the conjugate forces. The fluxes and forces may also be expressed by noting that the entropy is a function of various parameters, $\alpha_1, \alpha_2 \ldots$. The rate of production of entropy within the system is

$$dS_i/dt = \Phi/T = \sum_k (\partial S/\partial\vec{\alpha}_k)(d\vec{\alpha}_k/dt) \qquad (13)$$

Then the quantities $(\partial S/\partial\alpha_k) = X_k$ have the dimensions of forces and the $d\vec{\alpha}_k/dt = \vec{J}_k$ are the conjugate fluxes.

A central postulate of the Thermodynamics of Irreversible Processes is now introduced: The fluxes $\vec{J}_i$ are assumed to be homogeneous linear functions of the conjugate forces $\vec{X}_i$. That is,

$$\vec{J}_i = \sum_k L_{ik} \vec{X}_k \qquad (14)$$

where the phenomenological coefficients L_{ik} are assumed to be independent of the forces. According to Curie's theorem (1894), entities whose tensorial rank differ by an odd number will not interact in an isotropic system. Therefore, the vectorial fluxes can be functions only of the vectorial forces. On the other hand, scalar second rank tensor forces and fluxes can interact (stress tensors and chemical reactions). We will omit consideration of systems involving stress or chemical reactions. Under these circumstances Eq. (14) deals only with the vectorial forces and fluxes.

The fluxes to be used in this theory are the time derivatives of the thermodynamic variables used to express the entropy of the system in quadratic form and the forces conjugate to them are the derivatives of the entropy with respect to the corresponding thermodynamic variables. (L. Onsager, 1931). Examples of conjugate sets of forces and fluxes are given below.

As a final postulate of the Thermodynamics of Irreversible Processes, it is assumed that the matrix of the phenomenological coefficients, L, is symmetrical, i.e.

$$L_{ik} = L_{ki} \qquad (15)$$

These are the Onsager reciprocal relations (Onsager, 1931; Casimir, 1945). This postulate may be derived from the principle of microscopic

reversibility or may be regarded as a postulate obtained by empirical generalization comparable with the second law of thermodynamics.

In order to obtain the phenomenological equations in a form suitable for discussing fused salt systems a form must be chosen for the fluxes and forces in terms of which the dissipation function (Eq. 9) is to be expressed. We first consider some of the possible formulations at length. A comparison is given at the end of this section.

In an electrochemical system of n-1 neutral components, (without viscous forces or homogeneous chemical reactions) the behavior of the system can be described in terms of the fluxes of n-1 components plus the electrical current density plus the heat current density. Alternatively, n ionic (or at any rate not all neutral) fluxes plus the heat current density may be used. One may proceed to find the forces conjugate to either of these sets of fluxes according to the prescription given above and to construct the dissipation function. The proper sets of forces conjugate to these fluxes are

$$-\vec{\nabla}\,\psi \sim \vec{I}$$
$$-\vec{\nabla}_T \mu_i \sim \vec{J}_i \qquad\qquad i = 1,\ldots,n-1 \qquad\qquad (16)$$
$$-\vec{\nabla}\,\ln T \sim \vec{q}$$

for neutral components or

$$-\vec{\nabla}_T \tilde{\mu}_i = -\vec{\nabla}_T(\tilde{\mu}_i + z_i \widetilde{\mathcal{F}\psi}) \sim \vec{J}_i$$
$$\qquad\qquad\qquad i = 1\ldots n \qquad\qquad (17)$$
$$-\vec{\nabla}\ln T \sim \vec{q}$$

for ionic components. $\vec{\nabla}\psi$ may be conveniently measured in volts/cm, $\vec{I}$ in Faradays/cm²/sec, $\vec{\nabla}_T \tilde{\mu}_i$ in joules/mole/cm, $\vec{J}$ in moles/cm²/sec, T in degrees Kelvin and $\vec{q}$ in joules/cm²/sec.

We note that the Gibbs-Duhem relation for this system is

$$\sum_{i=1}^{n-1} c_i \vec{\nabla}_T \tilde{\mu}_i = -\vec{\nabla}p + \sum_k c_k \vec{F}_k = \rho \frac{d\vec{v}}{dt} = \sum_{i=1}^{n} c_i \vec{\nabla}_T \tilde{\mu}_i \qquad (18)$$

Here $\sum c_k \vec{F}_k$ represents the net external force density applied to the system. In a state of mechanical equilibrium $d\vec{v}/dt$ vanishes. For fused salt systems the interaction with bounding surfaces, porous plug diaphragms, etc. is often important. That is, the surface forces do not vanish. In this circumstance, the conservation of momentum equation in terms of the fluxes assumes the form

$$M_i \vec{J}_i = \vec{v} \sum c_i M_i + \int_0^t (c_i \vec{F}_i - \vec{\nabla}p)\, dt \qquad (19)$$

A number of phenomena of special interest in fused salt research appear to be connected with such forces and will be treated in Section VII. For the present, however, we assume surface and body forces and pressure gradients to be absent. Under these circumstances the forces and fluxes do not constitute independent sets of variables. If the velocities are measured with respect to the center of gravity ($\sum_i \vec{J}_i M_i = 0$), or the center of volume ($\sum_i \vec{J}_i \tilde{v}_i = 0$), or in a mole fixed system ($\sum_i \vec{J}_i = 0$) or indeed in any completely defined reference frame,

there will always be some relation among the matter fluxes, so that only n-1 of them are independent. Similarly, the Gibbs-Duhem equation will provide a relation among the n matter forces, leaving only n-1 of them independent. By eliminating one force and its conjugate flux with these relations an independent set of forces and fluxes can be obtained. This $\overset{can}{may}$ be done in a number of ways.

Suitable independent sets of conjugate forces and fluxes may be obtained by examination of the dissipation function. In terms of neutral components at uniform pressure this has the form

$$\Phi = - \sum_{k=1}^{n-1} \vec{J}_i \vec{\nabla}_T \mu_i - \vec{q} \vec{\nabla} \ln T - \vec{I} \vec{\nabla} \psi \tag{20}$$

where

$$\sum_{i=1}^{n-1} c_i \vec{\nabla}_T \tilde{\mu}_i = 0 \; ; \quad \sum_{i=1}^{n-1} \vec{J}_i M_i = 0 \tag{21}$$

The use of neutral components for describing conduction in an electrolytic system has been explored by Sundheim (1957) and will not be treated here. (cf. Section IV)

In terms of ionic components the dissipation function is

$$\Phi = - \sum_{k=1}^{n} \vec{J}_i \cdot \vec{\nabla}_T \chi_i - \vec{q} \vec{\nabla} \ln T \tag{22}$$

where

$$\sum_{i=1}^{n} c_i \vec{\nabla}_T \tilde{\mu}_i = 0 \qquad \sum_{i=1}^{n} \vec{J}_i M_i = 0$$

Eq. (22) may be written in terms of independent variables in two ways. On the one hand, the Gibbs-Duhem equation may be employed to eliminate a force:

$$\phi = - \sum_{k=1}^{n-1} \vec{J}_k \cdot \vec{\nabla}_T \tilde{\mu}_k - \vec{q} \, \vec{\nabla} \ln T + \vec{J}_n \cdot \sum_{k=1}^{n-1} (\frac{c_k}{c_n}) \vec{\nabla}_T \tilde{\mu}_k$$

$$= \sum_{k=1}^{n-1} (\vec{J}_k - \frac{c_k}{c_n} \vec{J}_n) \vec{\nabla}_T \tilde{\mu}_k - \vec{q} \cdot \vec{\nabla} \ln T \tag{23}$$

(The summation may also be written to n since this term automatically vanishes.) Hence the set of fluxes $\vec{J}_i^{(n)} = \vec{J}_i - c_i/c_n \, \vec{J}_n = c_i(\vec{v}_i - \vec{v}_n)$ together with $\vec{q}$ is conjugate to the forces $\vec{\nabla}_T \tilde{\mu}_i$ ($i = 1 \ldots n-1$) and $\vec{\nabla} \ln T$.

The forces and fluxes being independent, we may now write

$$\vec{\nabla}_T \tilde{\mu}_i = - \sum_{k=1}^{n-1} \bar{R}_{ik}^{(n)} c_k(\vec{v}_k - \vec{v}_n) - \bar{R}_{i,n+1}^{(n)} \vec{q}$$

$$\vec{\nabla} \ln T = - \sum_{k=1}^{n-1} \bar{R}_{n+1,k}^{(n)} c_k(\vec{v}_k - \vec{v}_n) - \bar{R}_{n+1,n+1}^{(n)} \vec{q} \tag{24}$$

$$i = 1 \ldots, n-1$$

and the Onsager reciprocal relations hold among the $\bar{R}_{ik}^{(n)}$ so that

$$\bar{R}_{ik}^{(n)} = \bar{R}_{ki}^{(n)} \tag{25}$$

Since the heat flux $\vec{q}$ is not often an independent variable, it is convenient to solve explicitly the last of Eq. (24) for $\vec{q}$ and substitute it into the first of Eq. (24)

$$\vec{q} = \left\{ - \sum_{k=1}^{n-1} \bar{R}_{n+1,k}^{(n)} c_k(\vec{v}_k - \vec{v}_n) + \bar{R}_{n+1,n+1}^{(n)} \vec{\nabla} \ln T \right\} \Big/ \bar{R}_{n+1,n+1}^{(n)}$$

so that

$$\vec{\nabla}_T \tilde{\mu}_i = - \sum_{i=1}^{n-1} R_{ik}^{(n)} c_k(\vec{v}_k - \vec{v}_n) - R_{i,n+1}^{(n)} \vec{\nabla} \ln T \tag{26}$$

where

$$R_{ik}^{(n)} = R_{ik}^{(n)} - \frac{R_{i,n+1}^{(n)} \; R_{n+1,k}^{(n)}}{R_{n+1,n+1}^{(n)}} \qquad (20a)$$

and hence

$$R_{ik}^{(n)} = R_{ki}^{(n)}$$

In fused salt systems, there is rarely a component that is uniquely suited to serve as solvent. All components enter on a more or less equal footing. It is convenient, therefore, to seek a more symmetrical representation. Noting that no coefficients R_{ik} with either i or k = n occur in Eq. (26), one is at liberty to introduce the definitions of these coefficients by the relations

$$\sum_{k=1}^{n} c_k R_{ik} = 0 \qquad R_{in} = R_{ni} \qquad i = 1 \ldots n+1 \qquad (27)$$

$$\vec{\nabla}_T \tilde{\mu}_i = - \sum_{k=1}^{n} R_{ik} \vec{J}_k - R_{i,n+1} \vec{\nabla} \ln T \qquad (28)$$

The definitions (27) were chosen to preserve the relations $R_{ik} = R_{ki}$; i,k = 1...n. It may be readily seen that they are equivalent to the statement that the addition of a uniform velocity to all the $\vec{v}_i$ does not affect the dissipation function (Onsager, 1957). Finally we may display Eq. (28) in still another form by the use of Eq. (27):

$$\vec{\nabla}_T \tilde{\mu}_i = - \sum_{k=1}^{n} R_{ik} \vec{J}_k - (\vec{J}_i/c_i) \sum_{k=1}^{n} R_{ik} c_k - R_{i,n+1} \vec{\nabla} \ln T$$

$$\vec{\nabla}_T \tilde{\mu}_i = - \sum_{k=1}^{n} R_{ik} c_k (\vec{v}_k - \vec{v}_i) - R_{i,n+1} \vec{\nabla} \ln T \tag{29}$$

In the last of Eq. (29) we see that the expressions for $\vec{\nabla}_T \tilde{\mu}_i$ are independent of the reference point chosen for the velocities. Laity (1959) has suggested that this is a significant advantage and has recommended that transport phenomena be described in terms of this type of "friction coefficient" (cf. also Spiegler, 1959 and Klemm, 1953). He has used the definition

$$r_{ik} = -R_{ik} \sum_{i=1}^{n} c_i \tag{30}$$

so that Eq. (29) becomes

$$\vec{\nabla}_T \tilde{\mu}_i = \sum_{k=1}^{n} r_{ik} x_k (\vec{v}_k - \vec{v}_i) \tag{31}$$

if the equivalent fraction of species k is designated by x_k.

Another method of selecting an independent set of forces and fluxes to express the dissipation function (Eq. 22) can be obtained by introducing the statement that the velocities are measured with respect to the local center of gravity to eliminate one of the forces. Then

$$\Phi = - \sum_{k=1}^{n-1} \vec{J}_k \cdot (\vec{\nabla}_T \tilde{\mu}_k - \frac{M_k}{M_n} \vec{\nabla}_T \tilde{\mu}_n) - \vec{q} \cdot \vec{\nabla} \ln T \tag{32}$$

where M_k is the mass per unit concentration of k.

We may then write the set of phenomenological equations in terms of the n-1 independent forces $(\vec{\nabla}_T \tilde{\mu}_k - (M_k/M_n)\vec{\nabla}_T \tilde{\mu}_n)$ and $\vec{\nabla} \ln T$ and the n-1 fluxes $\vec{J}_i (i=1...n-1)$ and $\vec{q}$.

$$\vec{J}_i = - \sum_k L_{ik} (\vec{\nabla}_T \tilde{\mu}_k - \frac{M_k}{M_n}\vec{\nabla}_T \tilde{\mu}_n) - L_{i,n+1} \vec{\nabla} \ln T \qquad (33)$$

Again noting that the subscript n does not appear in any of the coefficients, we may find a more symmetrical respresentation by introducing the definitions

$$\sum_{k=1}^{n} M_k L_{ik} = 0; \quad i = 1...n,n+1$$

$$L_{in} = L_{ni}; \quad i = 1...n,n+1 \qquad (34)$$

so that

$$\vec{J}_i = - \sum_{k=1}^{n} L_{ik} \vec{\nabla}_T \tilde{\mu}_k - L_{i,n+1} \vec{\nabla} \ln T \qquad (35)$$

(The definition (34) expresses the fact that the dissipation function Φ is not affected by application of a uniform body force to the system.)

Equation (35), which expresses the $\vec{J}_i$ in terms of the $\vec{\nabla}_T \tilde{\mu}_i$ and $\vec{\nabla} \ln T$ is a parallel form to Eqs. (28) and (29) which express the $\vec{\nabla}_T \tilde{\mu}_i$ in terms of the J_k or the $(\vec{v}_k - \vec{v}_i)$. The latter form is preferred by some workers since it is felt that the interference of forces due to relative motion of ions is easier to picture than the interference of fluxes due to the interaction of the forces. The former has some advantage in simplicity of manipulation, particularly for

multicomponent systems. A further comparison is given below.

It is possible to invert Eq. (35) to obtain Eq. (28), provided proper allowance is made for the dependence of the variables (Helfand, 1960). The interested reader is referred to this paper for the somewhat complicated relation between the R_{ik} and the L_{ik}.

C. Electrical Conductivity.

The isothermal electrical current density $\vec{I}$ in terms of the L_{ik} is

$$\vec{I} = \sum_{i=1}^{n} z_i \mathcal{F} \vec{J}_i = \sum_{i=1}^{n} z_i \mathcal{F} \left[\sum_{k=1}^{n} L_{ik} \vec{\nabla}_T \vec{\mu}_k + L_{i,n+1} \vec{\nabla} \ln T + c_i \vec{v}_o \right] \quad (36)$$

Of course I is independent of the reference point chosen for the velocity $(\vec{v}_o \sum_{i=1}^{n} c_i z_i = 0)$. The specific electrical conductivity κ is

$$\kappa = I/\nabla \psi$$

$$= 1/\mathcal{F}^2 \sum_{i,k} z_i z_k L_{ik}$$

The transference number of an ionic species t_i with respect to a reference point is defined as the number of equivalents of that species passing the reference point per Faraday of charge passed through the cell. Therefore

$$t_i = z_i \mathcal{F} \vec{J}_i / \vec{I} \quad (38)$$

The transference concept may be extended to neutral components by use of the Washburn number, w_i (E.W. Washburn, 1909). In the present case w_i in a uniform system may be defined as the number of formula weights

of i crossing the reference plane per mole of positive electricity passing through the cell in the same direction. For ionic species $t_i = z_i w_i$. In a uniform system the transference number may be expressed as

$$w_i = t_i/z_i = \mathcal{F}(c_i \vec{v}_0 + \sum_k L_{ik} z_k \mathcal{F} \vec{\nabla} \mathcal{V})/\vec{I}$$

$$= \sum_k z_k L_{ik} / \sum_{i,k} z_i z_k L_{ik} + \delta t_i/z_i \qquad (39)$$

where

$$\delta t_i = z_i \mathcal{F} c_i \vec{v}_0/\vec{I}$$

If the reference point is the local center of gravity, so that when $v_0 = 0$, $\delta t = 0$. We designate this transference number by the subscript zero so that

$$t_i = t_i^o + \delta t_i$$

For the particular case of a one component, two species fused salt, it is readily shown with the aid of Eq. (34) (Sundheim, 1956), that

$$t_2^o = \frac{M_1}{M_1 + M_2} \qquad (40)$$

(In this system there is only one independent phenomenological coefficient, L_{12}, and since it appears both in the numerator and denominator of Eq. (39), it does not appear in Eq. (40).)

In view of the relation $\sum_k t_k^o = 1$ and that $\sum_i M_i \vec{J}_i = 0$

so that $\sum_i M_i t_i^0 / z_i = 0$, a system of n ionic species is characterized by only n-2 independent transference numbers. The electrical conductivity itself, as expressed in Eq. (37), increases the number of independently measureable quantities to n-1.

The transference numbers reported in the literature are not generally measured with respect to the local center of gravity, but rather in cell-fixed or porous plug reference frames, so that δt must be determined from the conditions of the experiment. Substituting Eq. (39) into Eq. (36), for an isothermal system which is not of uniform composition, we can write:

$$\vec{\nabla}\psi = \vec{I}/\kappa - \sum_{k=1} (t_k/z_k)\tilde{\vec{\rho}}\vec{\nabla}_T\mu_k \qquad (41)$$

That is, the potential (measured between identical reversible electrodes) is the IR drop plus the so-called "~~diffusion~~ junction potential," the second term in Eq. (41). We note that the reference point chosen for the t_k in Eq. (41) is of no importance, since

$$\sum_k \vec{\nabla}_T\mu_k \ (t_k^0 + \delta t_k)/z_k = \sum_k t_k^0 \vec{\nabla}_T\mu_k + (\vec{v}_0/\vec{I})\sum_k c_k\vec{\nabla}_T\mu_k$$

$$= \sum_{k=1} \vec{\nabla}_T\mu_k t_k^0 \qquad (42)$$

These equations may also be cast in terms of the R_{ik}.

$$\vec{\nabla}_T\tilde{\mu}_i = -\sum_k R_{ik}\vec{J}_k - R_{i,n+1}\vec{\nabla}\ln T$$

$$\vec{J}_k = (t_k/z_k\tilde{\vec{\rho}}) \cdot \vec{I}$$

so that

$$\vec{\nabla} \psi = - \frac{1}{z_i \mathcal{F}} \left[\sum_k R_{ik} \left(\frac{t_k}{z_k \mathcal{F}} \right) I + R_{i,n+1} \vec{\nabla} \ln T \right]$$

(43)

$$\mathbf{k} = I / \vec{\nabla} \psi = - \left[\mathcal{F}^2 / \left(\sum_k R_{ik} t_k / z_i z_k \right) \right]$$

In the particular case of the isothermal conductivity of a two species, one component salt, Eq. (43) reduces to

$$\mathbf{k} = -z_\alpha z_\beta \mathcal{F}^2 / R_{\alpha\beta}$$

(44)

The equivalent conductivity λ is $\mathbf{k}/(c_i z_i)$.

D. **Diffusion.**

When the composition of the system is not uniform and the electrical current density vanishes, ordinary diffusion can occur. Returning to Eq. (36), we see that this implies that

$$\sum_i J_i = 0 = \sum_{i,k} z_i z_j \mathcal{L}_{ij} \nabla_T \tilde{\mu}_j + \sum_i z_i \mathcal{L}_{i,n+1} \nabla \ln T$$

(45)

Thus the forces and fluxes are no longer independent sets. The relation (45) must be maintained among them.

The definition of diffusion coefficients in fused salts requires particular attention. In dilute solutions of unionized solvents, a convenient reference frame for changes in composition is provided by the solvent itself. Also, there is no ambiguity about identifying the appropriate variables (unless there is a dissociative equilibrium). This "natural" reference frame afforded by the solvent is ordinarily not available in a fused salt. Furthermore, intuition suggests and some models require description in terms of the individual

ionic species. Since the motions of the ions are restricted by the requirement of electroneutrality, we must either note relations among the ionic diffusion coefficients or else combine the ions to form neutral components for which independent diffusion coefficients may be defined. It is necessary to consider the possible choices of independent variables, the number of phenomenological coefficients needed to describe the system and the relations between the various quantities of transport that may be encountered. (Kirkwood, et al., 1960; Sundheim, 1957).

We begin by expressing the flow equations in terms of electrically neutral combinations of charged ionic species. There are n ionic species so that only n-1 neutral components (independent composition variables) are required to describe the system at all points. In systems of two or three ionic species, the choice of components is straightforward. Thus, for Na^+ and Cl^- we use NaCl; for Na^+, K^+ and Cl^-, we may use NaCl and KCl as components. Where there are more than three ionic species the components may be chosen in several equivalent ways. Thus, in a system containing Li^+, Na^+, Cl^- and Br^- the components might be any three of LiCl, LiBr, KCl and KBr. For example, if LiCl, LiBr and KCl were the components used, then C moles/cc of KBr could be represented as C moles/cc of KCl + C moles/cc of LiBr-C moles/cc of LiCl. In general, we may write the flows $\vec{J}_K$ in terms of the flows, $\vec{J}_{kl}$, of the neutral component formed from species k and species l as

$$\vec{J}_i = \sum_l z_l \vec{J}_{kl} \tag{46}$$

where the sum runs over the n-1 components of formulae $(K^{z_+})_{z_-} (L^{z_-})_{z_+}$ and the z_l are the algebraic valences. The corresponding concentrations may be written by replacing the $\vec{J}$'s by c's in Eq. (46). The flow equations can be written in terms of the neutral combinations by expressing the chemical potential of the neutral components μ_{ij} in terms of those of the ionic species and then using Eqs. (28) and (46) (Kirkwood et al., 1960).

$$\vec{\nabla}_T \mu_{ij} = z_j \vec{\nabla}_T \tilde{\mu}_i - z_i \vec{\nabla}_T \tilde{\mu}_j = - \sum_k (z_j R_{ik} - z_i R_{jk}) \sum_l z_l \vec{J}_{kl}$$

$$- (z_j R_{i,n+1} - z_i R_{j,n+1}) \vec{\nabla} \ln T \tag{47}$$

Noting that terms with k = 1 do not appear, we may rearrange the summation as follows:

$$\vec{\nabla}_T \mu_{ij} = \sum_{k=1}^{l=1} \sum_{l=2}^{s} (z_j R_{ik} - z_i R_{jk}) z_l \vec{J}_{kl}$$

$$+ \sum_{k=l+1}^{s} \sum_{l=1}^{s-1} (z_j R_{lk} - z_l R_{jk}) z_l \vec{J}_{kl} + (z_j R_{i,n+1} - z_i R_{j,n+1}) \vec{\nabla} \ln T \tag{48}$$

Noting that $\vec{J}_{kl} = \vec{J}_{lk}$ and that z_k and z_l must have opposite signs to form a neutral molecule, we interchange k and l in the second summation and obtain

$$- \vec{\nabla}_T \mu_{ij} = \sum_{k=1}^{l-1} \sum_{l=2}^{s} (R_{ij,kl}) \vec{J}_{kl} \tag{49}$$

where

$$R_{ij,kl} = (z_j R_{ik} - z_i R_{jk}) z_l + (z_i R_{jl} - z_j R_{il}) z_k \tag{50}$$

and it may be seen that $R_{ij} = R_{ji}$ implies immediately that $R_{ij,kl} = R_{kl,ij}$ and also that $\sum_{i,j} c_{ij} R_{ij,kl} = 0$.

These equations are suitable for the description of diffusion without further concern about electroneutrality.

The conventional description of diffusion in a two component liquid system (e.g. Tyrrell, 1961) begins with Fick's Law in the form

$$\vec{J}_A = - D_A \vec{\nabla} c_A$$

$$\vec{J}_B = - D_B \vec{\nabla} c_B$$

(51)

If the reference plane for the fluxes is properly selected, the diffusion coefficients D_A and D_B can be made equal to each other. This common value is termed the mutual diffusion coefficient, D_{AB}, if the concentrations are measured in moles/unit volume and the fluxes in moles/unit area · unit time; the proper reference frame is one across which there is no change of volume ("volume-fixed") and is defined by

$$\vec{J}_A^V \tilde{v}_A + \vec{J}_B^V \tilde{v}_B = 0$$

(52)

Noting that $\tilde{v}_A c_A + \tilde{v}_B c_B = 1$, we find that $D_A^{(v)} = D_B^{(v)} = D_{AB}^{(v)}$ so that the diffusion process is completely described by

$$\vec{J}_A^{(v)} = - D_{AB}^{(v)} \vec{\nabla} c_A$$

$$\vec{J}_B^{(v)} = - D_{AB}^{(v)} \vec{\nabla} c_B$$

(53)

On the other hand, if the reference plane is that of the

local center of gravity ("mass-fixed")

$$\vec{J}_A^{(M)} = - D_{AB}^{(M)} (\rho/M_A) \nabla w_A$$

$$\vec{J}_B^{(M)} = - D_{AB}^{(M)} (\rho/M_B) \nabla w_B$$

(54)

$$w_A = M_A c_A / (M_A c_A + M_B c_B)$$

$$M_A \vec{J}_A + M_B \vec{J}_B = 0$$

whereas if the reference plane is such that the number of moles on each side remains constant ("number-fixed")

$$\vec{J}_A^{(N)} = - D_{AB}^{(N)} c \nabla N_A$$

$$\vec{J}_B^{(N)} = - D_{AB}^{(N)} c \nabla N_B$$

(55)

$$c = c_A + c_B$$

$$N_A = c_A / (c_A + c_B)$$

$$\vec{J}_A^{(N)} = \vec{J}_B^{(N)} = 0$$

The relation between the fluxes (moles/cm^{2}sec) measured with respect to the various planes is as follows:

$$\vec{J}_A^{(N)} = \vec{J}_A^{(M)} \cdot (M_1 N_1 + M_2 N_2)/M_2$$

$$\vec{J}_A^{(v)} = \vec{J}_A^{(M)} \cdot \tilde{v}_B / (\tilde{v}_A w_A + \tilde{v}_B w_B)$$

(56)

By application of these relations to Eq. (53), (54) and (55) it can be readily seen that

$$D_{AB}^{(V)} = D_{AB}^{(M)} = D_{AB}^{(N)}$$

(57)

Thus mutual diffusion is equally well described in any of these three coordinate systems (and indeed in any other which is linearly related to them) by properly selecting the units of concentration. It is important that the concentration units appropriate to e.g. the number-fixed reference plane, should not be used with the volume-fixed plane, since the coefficients defined in this way would then be different for each of the two species.

The expression for D_{12} in terms of the R_{ik} can be found by recasting Eq. (49) in terms of the diffusion coefficient. Substituting

$$\vec{\nabla}_T \mu_{13} = - (RT/X_{13}) \left[1 + (\partial \ln \gamma_{13}/\partial \ln X_{13}) \right] \cdot \vec{\nabla} X_{13} \qquad (58)$$

and Eq. (56) into Eq. (49) we obtain

$$\vec{J}_{13}^{(N)} = - RT/\left[R_{13,23}(c_1+c_2) \right] \cdot \left[1 + (\partial \ln \gamma_{13}/\partial \ln X_{13}) \right] \vec{\nabla} X_{13} \qquad (59)$$

hence we can identify

$$D_{12} = D_{12}^{(N)} = D_{12}^{(v)} = D_{12}^{(M)} = RT/(c_1+c_2) \left[1 + (\partial \ln \gamma_{13}/\partial \ln X_{13}) \right]/R_{13,23} \qquad (60)$$

The mutual diffusion coefficient may also be expressed in terms of the R_{ik}. With the aid of Eq. (50) we find

$$R_{13,23} = z_3(z_3 R_{12} - z_1 R_{23}) + z_2(z_1 R_{33} - z_3 R_{13}) \qquad (61)$$

A case of particular interest arises when the species 1 is a tracer for species 2. Then D_{12} is D_{12}^* the tracer diffusion coefficient of

species 2. Because 1 and 2 are considered to be chemically equivalent we may set $z_1 = z_2$ and $R_{13} = R_{23}$, and $(\partial \ln \gamma_{13} / \partial \ln X_{13}) = 0$. Then

$$R_{13,23} = z_3(z_1 R_{12} - z_3 R_{23})\qquad(62)$$

If $c_1 = c_2$ and the relation $\sum_i c_i R_{ik} = 0$ is employed, this may also be expressed as

$$R_{13,23} = z_3^2(R_{12} - R_{22})$$

Thus $D_{12}^* = D_2^* = RT / \left[(c_1 + c_2)z_3(z_1 R_{12} - z_3 R_{23})\right] = RT / \left[c_2 z_3^2(R_{12} - R_{22})\right]$

The factor z_3 arises as the number of formula weights of species 2 in the component between species 2 and species 3. The usual definition of the self diffusion coefficients omit this factor. The same treatment may be applied to any number of components. Thus for 3 ionic species the self diffusion coefficients can be obtained from consideration of a 3 component (4 species) system in which one species is a tracer for another. We find for example

$$D_{11}^* = - \frac{RT \left[z_1 z_2 c_T + c_{13} z_2 z_3 + c_{23} z_1 z_3\right]}{z_2 z_3 c_{13} R_{11} + z_1 z_3 c_{23} R_{13} + z_1 z_2 R_{13} c_T}\qquad(63)$$

Laity (1959) has observed that this expression has the form of the reciprocal of the average value of the friction coefficient of the diffusing ion against each of the ions it encounters. It should be noted particularly that a self diffusion coefficient is not directly expressed as a friction coefficient and vice-versa.

E. Practical Diffusion.

1. Frames of reference

The relations between the various practical diffusion coefficients and the most useful theoretical quantities are simple for systems of a few components but rapidly increase in complexity

as the number of components increases. We will first discuss the
general multicomponent system and then give the specific results
for a few systems. Then we will be in a position to discuss the
determination of friction coefficients from experimental data.

The theoretical equations useful in a general discussion
of transport properties express the flow of each component i as a
sum of forces (negative gradients of electrochemical potentials)
each multiplied by a diffusion coefficient L_{ik} (Eq. 35). In the
isothermal isobaric case these take the form:

$$\vec{J}_i = \sum_k L_{ik} \vec{X}_k \tag{64}$$

In experimental studies, flow equations are customarily written as
the sum of concentration gradients, each multiplied by a diffusion
coefficient D_{ij} of a different type. The L_{ik} are referred to as
"fundamental diffusion coefficients" (or somewhat inaccurately as
"thermodynamic diffusion coefficients") and the D_{ij} as "practical
diffusion coefficients."

The various diffusion coefficients may be written in many
different ways depending upon the reference frame adopted and on the
way in which the restrictive conditions are incorporated. In
Eq. (35) the system is described in terms of the n^2 quantities L_{ij}
(fundamental diffusion coefficients of the ionic species in the
mass-fixed frame of reference). Similarly, another set of $(n-1)^2$
fundamental mass-fixed diffusion coefficients, $L_{ij,kl}$, may be obtained
via Eq. (46) and the equivalent of Eq. (35) for neutral components.
Both of these sets deal with flows relative to the center of gravity. We must

now examine the effect on these quantities of changing the reference point.

The basic relation is simply $(\vec{J}_i)_R = (\vec{J}_i)_S + c_i\vec{v}_{SR}$. This equation relates the flux in frame of reference R to that in frame S by use of the velocity $\vec{v}_{SR}$ of frame S with respect to frame R at the position and time considered. The reference frames of particular interest are those with respect to the center of gravity (mass-fixed, subscript M), with respect to a particular component (solvent-fixed, subscript o), with respect to a frame moving so that no volume change occurs across it (volume - fixed, subscript V), with respect to the closed end of a cell (cell-fixed, subscript C) and with respect to a porous plug (plug-fixed, subscript P).

Volume-fixed frame. The following discussion is based on that of Kirkwood, Baldwin, Dunlop, Gosting and Kegeles (1960) to which reference should be made for a more complete treatment and for reference to other studies.

We begin with Eq. (65) where the subscripts refer to ionic components and it is known that $L_{ik} = L_{ki}$

$$\vec{J}_i^M = \sum_{k=1}^{n} L_{ik} \vec{\nabla}_T \mu_k \tag{65}$$

If one of the ionic components is chosen as reference (subscript o) then the use of the relation $\vec{v}_{Mo} = - \vec{J}_o^M /c_o$ and the Gibbs-Duhem equation, $\sum_i c_i \nabla_T \mu_i = 0$ converts this to

$$\vec{J}_i^o = \sum_{\substack{k=1 \\ \neq o}}^{n} L_{ik}^o \vec{\nabla}_T \mu_k \tag{66}$$

where

$$L_{ik}^{o} = L_{ik} - \frac{c_i}{c_o} L_{ok} - \frac{c_k}{c_o} L_{oi} + \frac{c_i c_k}{c_o^2} L_{oo}$$

The relation $L_{ij}^{o} = L_{ji}^{o}$ is still preserved among the $(n-1)^2$ coefficients. The practical diffusion coefficients in the reference frame determined by species o can now be obtained by expressing the gradients of the chemical potentials in terms of concentration gradients. Since there are only $(n-2)$ independent composition variables this may be done by writing

$$\vec{\nabla}_T \tilde{\mu}_i = \sum_{k=1}^{n-2} (\partial \mu_i / \partial c_k) \vec{\nabla} c_k \qquad i=1...n-2 \tag{67}$$

then

$$J_i^{o} = - \sum_{k=1}^{n-2} D_{ik}^{o} \vec{\nabla} c_k \qquad i=1...n-2 \tag{68}$$

where

$$D_{ik}^{o} = \sum_{j=1}^{n-2} L_{ij}^{o} (\partial \mu_j / \partial c_k) \tag{68}$$

The relations for obtaining the L_{ik}^{o} from measurements on the D_{ik}^{o} can be found by inverting the last equation

$$L_{ik}^{o} = |\partial \mu / \partial c|_{ik} / |\partial \mu / \partial c| \tag{70}$$

Here $|\partial \mu / \partial c|$ is the determinant of the matrix of the $\partial \mu_i / \partial c_k$ and $|\partial \mu / \partial c|_{ik}$ is the sum of the appropriate minors multiplied by the

corresponding D_{ik}^o . For $n = 4$ (three neutral components of which one is designated as solvent), these equations are

$$L_{11}^o = [D_{11}^o\,(\partial\mu_2/\partial c_2) - D_{12}^o\,(\partial\mu_2/\partial c_1)]\,/S$$

$$L_{12}^o = [D_{12}^o\,(\partial\mu_1/\partial c_1) - D_{11}^o\,(\partial\mu_1/\partial c_2)]\,/S$$

$$L_{21}^o = [D_{21}^o\,(\partial\mu_2/\partial c_2) - D_{22}^o\,(\partial\mu_2/\partial c_1)]\,/S \tag{71}$$

$$L_{22}^o = [D_{22}^o\,(\partial\mu_1/\partial c_1) - D_{21}^o\,(\partial\mu_1/\partial c_2)]\,/S$$

$$S = (\partial\mu_1/\partial c_1)\,(\partial\mu_2/\partial c_2) - (\partial\mu_1/\partial c_2)\,(\partial\mu_2/\partial c_1)$$

The solvent-fixed frame is not often of primary interest for fused salt systems but may be used conveniently to obtain the volume-fixed equations.

The velocity of the volume-fixed frame relative to the solvent-fixed frame is $\vec{v}_{oV} = -\sum_{i=1}^{n-2} \tilde{v}_i\,\vec{J}_i^o$ so that

$$\vec{J}_i^V = \vec{J}_i^o - c_i \sum_{j=1}^{n-2} \tilde{v}_j\,\vec{J}_j^o \tag{72}$$

When this is inserted into Eq. (66), the set of flow equations is found

$$\vec{J}_i^V = - \sum_{k=1}^{n-2} D_{ik}^V\,\vec{\nabla} c_k \qquad i = 1\ldots n-1 \tag{73}$$

where

$$D_{ik}^{V} = D_{ik}^{o} - c_i \sum_{j=1}^{n-1} \tilde{v}_j D_{jk}^{o} \tag{74}$$

$$i,k = 1...n-1$$

The inverted expression which may be used to obtain D_{ik}^{o} from the measured D_{ik}^{V} is

$$D_{ik}^{o} = D_{ik}^{V} + (c_i/c_o\tilde{v}_o) \sum_{j=1}^{n-1} \tilde{v}_j D_{jk}^{o} \qquad i,j = 1...n-1 \tag{75}$$

Cell-fixed frame. If the partial specific volumes of the various components $\tilde{v}_i$ change with composition, the process of diffusion will be accompanied by a volume change. The net flow brought about by this volume change will not affect the diffusion equations for the M, O and V frames of reference. However, if the frame of reference is the closed end of the cell then the liquid at each point experiences a hydrodynamic flow due to the volume change between that point and the end of the cell. Since this flow varies with position in the cell, the resulting equations of motion are not simple. Kirkwood et al. (1960) have shown that the equations of flow in a rectangular cell, closed at bottom and open at the top are

$$J_i^{(c)} = - \sum_{k=1}^{n-1} D_{ik}^{V} (\partial c_k/\partial x)$$

$$- c_i \int_{-\infty}^{x} \left\{ \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \sum_{\ell=1}^{n-1} (\partial \tilde{v}_j/\partial c_\ell)[D_{jk}^{V} + (c_j/c_o\tilde{v}_o). \right. \tag{76}$$

$$\left. \cdot \sum_{m=1}^{n-1} \tilde{v}_m D_{mk}^{V}] (\partial c_k/\partial x)(\partial c_\ell/\partial x) \right\} dx$$

Procedures for obtaining the practical diffusion coefficients

from measured flows have not been worked out for the case where volume changes are considerable. If the volume changes are small and/or the concentration gradients are kept small then these flow equations become approximately those of the volume-fixed frame. Kirkwood et al. point out that the conventional procedures for treating experimental diffusion data in closed end cells lead to approximate values of the D_{ik}^V. (See, however, F.A.L. Dullien and L.W. Shemilt, 1962).

Plug-fixed frame. A further reference point which is of great interest in fused salt systems is the "plug-fixed" one. It is shown in Section V that $\vec{V}_{PM}$ is

$$\vec{V}_{PM} = - \sum_k \eta_k \vec{J}_k^M / \sum_k \eta_k \tag{77}$$

Consequently, the flow equations in this frame of reference are

$$\vec{J}_i^P = - \sum_{k=1}^{n-1} L_{ik} \vec{\nabla}\tilde{\mu}_k + c_1 \sum_l \eta_l \vec{J}_l^M / \sum_k \eta_k$$

$$= - \sum_{k=1}^{n-1} (L_{ik} + c_i \sum_l \eta_l L_{1l}) \vec{\nabla}\tilde{\mu}_k \tag{78}$$

$$= - \sum_{k=1}^{n-1} L_{ik}^P \vec{\nabla}\tilde{\mu}_k$$

~~quantities~~ L_{ik}

Note that the reciprocal relations do not in general hold among the quantities L_{ik}^P.

Conductance and transference numbers. In the absence of composition gradients the specific electrical conductivity, Λ, may be written as

$$\lambda = I/\vec{\nabla}\varphi = \sum_{k=1}^{n} z_i \vec{\mathscr{F}}\vec{J_i}/\vec{\nabla}\psi$$

$$= \sum_{k=1}^{n} z_i z_k L_{ik} \tag{79}$$

This conductivity is expressed in terms of the gradient of the "inner potential" and its relation to that expressed in terms of the "outer potential" needs to be noted.

The transference numbers in this frame of reference are

$$t_i = z_i \vec{\mathscr{F}}\vec{j_i}/\vec{I}$$

$$= z_i \sum_k z_k L_{ik}/\sum_k z_i z_k L_{ik} \tag{80}$$

The difference between inner and outer potential does not bear on the transference numbers but changes in reference point change the transference numbers although they do not affect the expression for the conductivity.

Since $\sum_{i=1}^{n} t_i = 1$, there are apparently n-1 transference number measurements possible plus one conductivity. However, the relation $\sum \vec{J_i} M_i = 0$ (or any similar relation identifying a reference velocity) makes it possible to express one of these in terms of the remaining ones so that only n-2 transference number measurements are actually independent. The two restrictions are

$$\sum_i (t_i/z_i) = \sum_{i,k} (z_k - z_i) L_{ik} = 0$$

$$\tag{81}$$

and $$\sum_i t_i = 1$$

The chain of transformations that leads from the friction coefficients to the practical diffusion coefficients is summarized in Table I.

As we have seen, there is a variety of formulations of the phenomenological equations of transport. The forces may be expressed in terms of the fluxes, the fluxes may be given in terms of the forces, the representation may be symmetrical or unsymmetrical (see Disc. Far. Soc. $\underline{32}$, 1961, pp. 172, 250), and for diffusion may be given in terms of ionic or neutral components. One may ask whether any particular formulation has something to recommend its use over the others. A comparison may be drawn as follows.

The expression in terms of the R_{ik} (or $r_{ik} = -c_T R_{ik}$) has the notable advantage that the non-diagonal terms ($i \neq k$) are independent of the frame of reference so long as it is linearly related to the center of gravity. Changes in the reference point lead only to changes in the diagonal terms. That is, the R_{ii} are different in mass-fixed, volume-fixed, etc. systems. Alternatively, we may abandon the form of Eq. (78) and restrict ourselves to the form of Eq. (24) so that the R_{ii} are completely unused and undefined. The tracer diffusion coefficients could then be used to calculate a set of diagonal terms, R_{ii}^*. If this is done, it should be noted that the electrical conductivity, mutual diffusion coefficients and transference numbers all can be calculated in terms of the non-diagonal R_{ik} and conversely the non-diagonal terms can be obtained from just these data (see below). However, the relation between the tracer diffusion coefficients and the diagonal elements involves the other coefficients.

The expression of the phenomenological equations in terms of the L_{ik} has the advantage of flexibility and convenience. The expressions for diffusion coefficients, transport numbers and conductivity in terms of the L_{ik} are simple. This is analogous to the simple combination of partial resistivities which leads to a combination of reciprocals. However changes in the L_{ik} with the reference point are not restricted to the diagonal terms.

The use of neutral combinations rather than ionic constituents is of great convenience in treating diffusion data but precludes the discussion of conduction and of transference in a symmetrical way. (See however, Sundheim, 1956, 1960).

On the balance, then, it would seem that the most suitable mode of representation for fused salt systems for theoretical purposes is the R_{ik} although other modes will doubtless continue to be used for special purposes.

F. Determination of Friction Coefficients.

Let us now turn our attention to the complementary problem; namely the determination of the friction coefficients from experimental quantities. Here the following problem presents itself: There are $(n-1)(n-2)/2$ experimentally determinable codiffusion coefficients which may be transformed into $(n-1)^2$ fundamental diffusion coefficients (e.g. volume-fixed). Among these latter, the $(n-1)(n-2)/2$ reciprocal relations are expected to hold together with $(n-1)$ relations arising from the identifications of the reference point. (The applicability of the reciprocal relations has been studied for several ternary solutions but not directly for fused salts. Nevertheless, we shall

assume that they are valid.) The number of ionic friction coefficients to be calculated is n^2 minus the n diagonal terms minus the $n(n-1)/2$ symmetry relations giving a total of $n(n-1)/2$ independent quantities. In general, therefore, there is an excess of $(n-1)$ independent quantities to be determined over the number of independent measurements available. Thus it is not possible to obtain the friction coefficients from diffusion data alone. The number of independent transference numbers that can be obtained is $(n-2)$ and together with electrical conductivity, this additional set of $n-1$ independent experimental quantities can be combined with the diffusion data to obtain all of the friction coefficients.

For example, in a one component, two species system, where $n = 2$, there is only the electrical conductivity to be determined. In a two component, three species system, one transport number (or combination of numbers), one interdiffusion coefficient and one electrical conductivity can be measured.

General expressions for obtaining the friction coefficients from experimental data may be expected to be extremely unwieldy. Specific relations for systems of two and three species are given below. (Experimental results for more complex systems have not been reported to date.)

Two Species:

$$R_{\cdot} = (z_{-} - z_{+})\mathcal{J}^2/(c_T \cdot \Lambda) \tag{82}$$

Three Species:

The explicit expressions are cumbersome. The implicit expressions (Laity, 1959) are

$$\Lambda = \frac{(\mathcal{F}^2/c_T)(z_1 z_2/z_3 - X_{13}z_2 - X_{23}z_1)(z_3 R_{12} - z_2 X_{23}R_{13}z_1 X_{13}R_{23})}{(z_1 z_2/z_3)R_{13} - z_1 X_{23}R_{12}R_{23} - z_2 X_{13}R_{12}R_{13}}$$

$$P = 1 - t_1 - t_3 X_{13}$$

$$= \frac{X_{23}(z_2 R_{13} - z_3 R_{12})}{z_1 X_{13}R_{23} + z_2 X_{23} - z_3 R_{12}} \tag{83}$$

$$D_{12} = \frac{(RT/c_T)\left[z_1 X_{23} + z_2 X_{13} - z_1 z_2/z_3\right]}{z_3 R_{12}(z_1 X_{23} + z_2 X_{13}) - z_2 X_{23}R_{13}[z_1 + (z_1 - z_2)X_{13}] - z_1 X_{13}R_{23}[z_2 + (z_1 - z_2)X_{23}]}$$

Tracer diffusion. The codiffusion coefficient between two components which differ only in isotopic composition is called the tracer diffusion coefficient (or, less accurately, the self-diffusion coefficient) of that component. For example, if a very small amount of $Na^{22}Cl$ is dissolved in $Na^{23}Cl$, the process of mutual diffusion of these components is describable by a single practical diffusion coefficient (if the solution is sufficiently dilute, the reference point is unimportant). Since such a solution is approximately ideal, the fundamental diffusion coefficient is readily found to be (Eq. 62):

$$D_A^* = RT\left[c_A z_B(z_A R_{AA}^* - z_B R_{AB}\right] \tag{84}$$

It has been suggested (Laity, 1959) that the friction coefficient found from this codiffusion coefficient be used to define the unmeasurable diagonal terms R_{ii}^*. However, the coefficients defined in this way may not be used in the diffusion equations

$$\vec{\nabla}_T \tilde{\mu}_i = \sum_k R_{ik}\vec{J}_k \tag{85}$$

since these are correct only if $R_{ik} = - \sum_{k \neq i} R_{ik} c_k / c_i$. It would seem

best to avoid such double usage for the coefficients R_{ii} (or r_{ii} or $\mathscr{G}_{ii}$).

This point is particularly important when one treats the migration of

one isotopic species with respect to another during electrolysis (Bearman, 1958).

However, since they are sometimes used, the relations between the R_{ii}^{*}

and the D_{A}^{*} are given here:

Two species:

$$R_{++}^{*} = (z_{+}/z_{-}) \, R_{\pm} + (z_{+} - z_{-})RT/(D_{+}^{*} \, z_{-} \cdot c_{T}) \qquad (84a)$$

$$R_{--}^{*} = (z_{-}/z_{+}) \, R_{\pm} + (z_{-} - z_{+})RT/(D_{-}^{*} \, z_{+} \cdot c_{T}) \qquad (84b)$$

Three species:

Again the implicit expressions are the simpler:

$$D_{1}^{*} = (RT/c_{T}) \frac{(z_{2}X_{13} + z_{1}X_{23} - z_{1}z_{2}/z_{3})}{z_{2}X_{13}R_{11}^{*} + z_{1}X_{23}R_{12} - z_{1}z_{2}R_{13}/z_{3}}$$

$$D_{2}^{*} = (RT/c_{T}) \frac{(z_{1}X_{23} + z_{2}X_{13} - z_{1}z_{2}/z_{3})}{z_{1}X_{23}R_{22}^{*} + z_{2}X_{13}R_{12} - z_{1}z_{2}R_{23}/z_{3}}$$

$$D_{3}^{*} = (RT/c_{T}) \frac{(z_{1}X_{23} + z_{2}X_{13} - z_{1}z_{2}/z_{3})}{z_{1}X_{23}R_{23} + z_{2}X_{13}R_{13} - z_{1}z_{2}R_{33}^{*}/z_{3}}$$

G. Motion within Porous Media.

In addition to the isopiestic experiments described above,

measurements on systems which include pressure gradients and hence

frictional interaction with a diaphragm of some sort, e.g. streaming

potentials, are particularly interesting in fused salts. It is useful,

therefore, to introduce explicitly the possibility of momentum transfer

between the electrolyte and the cell. (For further discussion of this

point see Section IB) We first treat the phenomenological description

of systems of this sort and then consider possible mechanisms

for such interaction.

The flow of a liquid through a cell containing a narrow channel or its percolation through a porous membrane is resisted by a force which depends on the relative velocity of the liquid and the cell. In the first approximation this force is directly proportional to the relative velocity so that, at low relative velocities, the restraining force per unit cross section may be written as

$$\vec{F} = - R(\vec{v} - \vec{v}_c)$$ (86)

where $\vec{v}$, $\vec{v}_c$ represent respectively the velocities of the liquid and of the cell with respect to the reference point. The proportionality constant R presumably depends on the structure of the cell. For a one component liquid, R is termed the flow resistivity of the porous medium. When the porous medium is equally resistant in all directions, R is a scalar; for non-isotopic materials it would be a dyadic. In the special case of the flow of a one component liquid through a single narrow tube, R is proportional to the viscosity of the liquid and inversely proportional to the square of the radius of the tube (Poiseuille, 1840, 1841; Hagen, 1839). In more complicated porous structures X is sometimes described as the product of the viscosity and a "tortuosity factor."

In concentrated aqueous electrolytic solutions, the viscosity of solutions may be approximately described in terms of modification of the viscosity of the solvent by hydrodynamic effects due to the distortion of the solvent streamlines in the liquid undergoing streaming motion by the obstruction represented by the ions (Einstein, 1906).

In a fused salt system which may be undergoing diffusion or conduction, and for which there is no well defined solvent species, it does not seem likely that a single viscosity coefficient can

describe all the modes of motion. Accordingly, we make the tentative
hypothesis that the force on the liquid can be written as the sum
of the forces on the various ionic species and that the frictional
force for each is porportional to its velocity relative to the cell.
That is,

$$F_i = - \sum_i R_i(\vec{v}_i - \vec{v}_c)$$

(97)

where each of the R_i may be expected to be dependent on the material
of construction and the geometry of the cell and on the composition
of the fused salt. (This general expression reduces to the more
usual one if all R_i tend to the same value.)

Furthermore, when there is a pressure gradient we must
take into account its effect on the volume changes accompanying ionic
migration and electrode reactions (we assume the electrolyte to be
incompressible). If the algebraic values of the volume changes per
Faraday due to the anodic and cathodic reactions are denoted respectively
as δv_A, δv_c (for identical electrodes $\delta v_A = - \delta v_c$) and if the
electrodes are placed in such a fashion that edge effects, etc. can
be ignored, then the terms which must be added to the dissipation
function because of the pressure gradient and the frictional inter-
action with the cell are

$$\sum_i \vec{v}_i(c_i - v_i c_i) \nabla p = [\delta v_A p_A + v_c p_c] I/F$$

(98)

$$+ \sum_i (\vec{v}_i - \vec{v}_c) z_i R_i(\vec{v}_i - \vec{v}_c)$$

The dissipation function now has the form

$$\Phi = \sum_i \vec{J}_i \vec{X}_i - \vec{q} \cdot \vec{\nabla} \ln T + (\vec{\sigma} + p\vec{1}) : \vec{\nabla}\vec{v} - \sum_k \Delta F_k \frac{d\lambda_k}{dt}$$

(89)

$$+ \sum_i R_i(\vec{v}_i - \vec{v}_c^0)(\vec{J}_i - \vec{v}_c c_i) - \sum_i \tilde{v}_i (\vec{J}_i) \cdot \vec{\nabla}p - (\delta v_A P_A + \delta v_c P_c) \vec{\nabla}|\vec{1}|$$

where $\vec{X}_i = -\vec{\nabla}_{T,p}\tilde{\mu}_i$.

In the absence of viscous forces and chemical reactions, this becomes

$$\Phi = \sum_i \vec{J}_i \cdot \left\{ \vec{X}_i - [\delta v_A P_A + \delta v_c P_c] z_i e (\vec{J}_i/|\vec{J}_i|) - \tilde{v}_i \vec{\nabla}p \right\} - \vec{q} \cdot \vec{\nabla} \ln T$$

(90)

$$+ \sum_i (\vec{J}_i - c_i \vec{v}_i) \cdot R_i (\vec{v}_i - \vec{v}_c)$$

If we further specialize by setting $\vec{\nabla} \ln T = 0$ and by choosing the porous medium itself as the reference point so that $\vec{v}_c \equiv 0$, then Eq. (90) can be written in the form

$$\Phi = \sum_i \vec{J}_i \vec{X}_i{}''$$

(91)

where

$$\vec{X}_i{}'' = \vec{X}_i - (\delta v_A P_A + \delta v_c P_c) z_i \mathscr{F} 1/|1| - \tilde{v}_i \vec{\nabla}p - R_i \vec{v}_i$$

The fluxes $\vec{J}_i$ are now written in the linear approximation as a combination of the "forces" $\vec{X}_i{}''$

$$\vec{J}_i = \sum_k L_{ik} \vec{x}_k^n$$

$$= \sum_k L_{ik} [\vec{x}_k - (\delta v_A p_A + \delta v_i p)(\vec{I}/|I|)z_i \tilde{\mathscr{F}} - \tilde{v}_i \vec{\nabla} p - R_i \vec{v}_i \qquad (92)$$

$$= [1/(1 + R_i/c_i)] [\sum_k L_{ik} \vec{x}_k] - \tilde{\mathscr{F}} [(\delta v_A p_A + \delta v_B p_B) \sum_k z_k L_{ik} \vec{\nabla} p / |\nabla p| - \vec{\nabla} p \sum_k L_{ik} \tilde{v}_k]$$

Thus the L_{ik} are seen to be the same quantities L_{ik} encountered in Eq. (14'). The effect of the frictional interaction with the walls then appears simply as the coefficient $\frac{I}{1+R_i/c_i}$, which now multiplies L_{ik} in the phenomenological equations.

The total force acting on an element of the fluid is

$$\sum_i c_i \vec{x}_i^n = \sum_i c_i \vec{x}_i - (\delta v_A p_A + \delta v_c p_c) \sum_i c_i z_i \tilde{\mathscr{F}} (J_i/|J_i|) - \vec{\nabla} p \sum_i c_i \tilde{v}_i + \sum_i R_i \vec{J}_i$$

$$= -\vec{\nabla} p + \sum_i R_i \vec{J}_i = \rho\, d\vec{v}/dt = 0$$

Therefore in the steady state we may write

$$\vec{\nabla} p = \sum_i R_i \vec{J}_i \qquad (93)$$

That is, the frictional force on the walls is balanced by the pressure gradient.

We may now examine some of the modes of motion of the system.

1. Percolative flow

If all $\vec{J}_i = c_i \vec{v}_T$, Eq. (93) becomes

$$\vec{\nabla} p = v_T \cdot \sum c_i R_i = R \vec{v}_T$$

where R is the flow resistivity of the system.

2. Electrical Conductivity

In a uniform system at zero pressure

$$I = - \sum_i \frac{z_i \tilde{\mathscr{F}}}{1 + R_i/c_i} \sum_k z_k \tilde{\mathscr{F}} \; \vec{\nabla} \psi \, L_{ik}$$

$$\lambda = - I/\nabla\psi = \tilde{\mathscr{F}}^2 \sum_{i,k} [z_i z_k L_{ik}/(1 + R_i/c_i)] \tag{94}$$

Using the subscript zero to denote the conductivity λ_o and the transference numbers t_o (see below) when the R_i vanish,

$$\lambda_o = \tilde{\mathscr{F}}^2 \sum_{i,k} z_i z_k \, L_{ik} \tag{95}$$

Then

$$\lambda/\lambda_o = \sum_i (t_i)_o/(1 + R_i/c_i) \tag{96}$$

In general the transference numbers t_i are all positive so that $\lambda < \lambda_o$. That is, the conductivity is expected to be reduced by the frictional interaction with the walls.

3. Transference

$$t_i = z_i \tilde{\mathscr{F}} \vec{J}_i/\vec{I} = [z_i/(1 + R_i/c_i)] \cdot \sum_k [z_k L_{ik}/ \sum_{i,k} z_i z_k L_{ik}/(1 + R_i/c_i)] \tag{97}$$

$$= [(t_i)_o/(1 + R_i/c_i)] / \sum_{i,k} [(t_i)_o/(1 + R_i/c_i)]$$

H. Porous Plug Reference Points

A reference point that may be adopted in diffusion or transference measurements is that defined by a porous plug, such as a sintered disc or an asbestos fiber. It is important to determine the relation

of this reference point to others, such as the mass-fixed or volume-fixed ones, in terms of microscopic parameters. A phenomenological description was given in Section G. Here we speculate about a possible mechanism for the establisment of the flow in a porous medium. An idealized representation of a Hittorf type transference cell is given in Fig. 1 (see, for example, the apparatus used by Duke and Laity (1954) or Bloom and Doull (1956). Here the plug represents the resistance to flow offered by a porous plug and or the walls of the cell.

During the isothermal electrolysis of a one component salt such as silver chbride, the movement of the ions and the electrode reactions produces volume changes in the electrode compartments. **However, the experiment is so designed that no pressure gradient** can occur. Since the system as a whole is electrically neutral, the uniform electrical field exerts no net force on the system (salt plus cell). There is no linear force component associated with the electrode reactions because streamlines from simple sources and sinks are symmetrical and radially directed. No net force being exerted on the system, the center of gravity will remain at rest during the experiment. The interaction between the salt and the cell as re-presented by the plug determines their relative motion which must be such as to leave the center of gravity of the entire system un-accelerated. During electrolysis the two ionic species are moving through the plug in opposite directions and the crux of the matter is the question: what is the net force (rate of transfer of momentum) between the salt and plug? If the force exerted by drag of negative

ions so that the center of gravity of the plug is motionless with respect to the center of gravity of the salt, then the plug will have the velocity (mass-average velocity) given by

$$\vec{v} = (M_A \vec{V}_A + M_B \vec{V}_B)/(M_A + M_B) \qquad (98)$$

where M_A, M_B are the formula weights of anion and cation respectively. It follows (Sundheim, 1957) that the transference number measured in such an experiment is given by a simple expression:

$$t_A = M_B/(M_A + M_B) \qquad (99)$$

The central hypothesis in this derivation is that a porous plug will assume the mass average velocity of the ions flowing through it. Comparison with experiment shows that the transference numbers obtained experimentally are often not in accord with the formula of Eq. (99). We may then conclude that there is a net transfer of momentum between the plug and the salt and must now re-examine the interaction between plug and salt.

Some possible sources of the forces exerted between the salt and the cell are:

1. Surface effects along the bounding line (Fig. 1). A study of the different experimental designs adopted by investigators indicates that variations in the size and shape of this perimeter do not appear to affect the measurements.

2. Specific interaction of the materials of construction with one of the ions. Experiments have been reported which show that the results are not changed by substituting quartz, alundum or similar materials for glass except in the immediate vicinity

of the softening point of the glass.

3. Electroösmosis: This term is ordinarily used to refer to the flow of the liquid through a tube or membrane accompanying the passage of electrical current. In dilute electrolytic solutions it is attributed to the action of the electrical field on the electrical double layers formed because of specific adsorption of one of the ionic species on the surface. The effect commonly falls off with increasing ionic strength. The independence of the nature of the wall and the high ionic strength militate against accepting this mechanism for fused salt systems. The phenomena might well be called electroösmosis but this labelling in itself does not improve our understanding since the mechanism involved apparently is quite different from that ordinarily associated with this name.

Although very systematic studies of the influence of materials of construction, pore size, current density and other variables have not been reported to date, nevertheless the experimental results suggest that the transfer of momentum between the porous plug and the molten salt is a phenomenon characteristic of the salt alone. We shall adopt that point of view in the discussion given in the remainder of this section.

In order to analyze more thoroughly the interaction between the salt and the wall, we first note that viscosity studies have shown that molten salts display Newtonian flow in viscometer capillaries. This implies that the salts, which wet all of the common construction materials, meet laminar boundary conditions; that is, the velocity of flow goes to zero as the wall is approached. We assume that

when the two kinds of ions are moving in different directions under
the influence of the electrical field the ionic velocities individually
approach zero at the wall. The transition between zero velocity at the
wall and the velocity observed from the wall must take place in a boundary
layer of unknown but presumably very small dimensions. It is our intention
to propose a mechanism for the flow in this boundary layer so as to link
the observed phenomena with some definite property of the salt.

The motion of the local center of gravity of the liquid with
respect to the wall may be grossly described by specifying an electro-
kinetic mobility, μ, defined by

$$\vec{v} = \mu \; \vec{\nabla} \psi \tag{100}$$

To accord with experiment this coefficient must be independent of
tube size, materials of construction, current density, etc. over the
range in which transference numbers appear to be independent of these
parameters.

Next we note that the laminar boundary conditions mean
that during electrolysis the ions in the boundary layer must be in
a state of shear, the positive and negative ions shearing in opposite
directions (Fig. 2). It is not unreasonable to assume that rate of
transfer of momentum between adjacent lamina may be different for
different kinds of ions.

A shearing force of this sort may be introduced into the
flow equations by adding the term

$$\vec{\nabla}\vec{\sigma}' = \sum_{k} \; (\varphi_{\alpha k} + \eta_{\alpha k}/3) \, \vec{\nabla}\vec{\nabla} \cdot \, J_{k} \tag{101}$$

to the stress tensor in the equation of motion. The new terms are
exactly analogous to the terms describing conventional viscosity.
Their form may be justified either by considerations of dimensional
analysis or by extension of the development of the stress tensor in
terms of perturbations to the distribution functions (Bearman, 1960;
Sundheim,1960; Klemm,1960). They have not been previously used in
description of liquid since it is (not) generally possible to apply
different forces to the various species as can be done by applying
a uniform electric field to a liquid electrolyte. Whenever the
peculiar velocities, $\vec{j}_i$, are zero, this contribution will vanish.

In order to describe the steady state, isothermal, isobaric
electrolysis of a liquid, Eqs. (2) and (101) are specialized to

$$0 = \eta_\alpha \nabla^2 \vec{v} + (\varphi_\alpha + \eta_\alpha/3)\, \vec{\nabla}\vec{\nabla}\cdot \vec{v} + \sum_k \eta_{\alpha k}\nabla^2 \vec{J}_k + \sum_k (\varphi_{\alpha k} + \eta_{\alpha k}/3)\vec{\nabla}\vec{\nabla}\cdot \vec{J}_k$$

$$- c_\alpha \vec{\nabla}_T(\mu_\alpha + z_e \varphi) - \sum_k f_{\alpha k}\,(\vec{J}_\alpha - \vec{J}_k)$$

(102)

For simplicity we treat a cell with walls parallel to the long dimension
(Fig. 1) and of arbitrary cross section. We imagine the electrodes
to be arranged so that all of the flow streamlines of all of the
species parallel to these walls. The volume changes produced at
the electrodes are imagined to be obviated by some external arrange-
ment. Under these conditions each of the velocity vectors will have
only its z (longitudinal) component different from zero and this
component itself will not be a function of z (in the region far

removed from the electrodes). Thereupon Eq. (102) becomes

$$\eta_\alpha \nabla^2 \vec{v} + \sum_k \eta_{\alpha k}\vec{J}_{\alpha k} \cdot c_\alpha \vec{\nabla}_T\tilde{\mu}_\alpha - \sum_k f_{\alpha k}(\vec{J}_\alpha \cdot \vec{J}_k) =$$

$$= \sum_k \left[(\varphi_{\alpha k} + \eta_{\alpha k}/3)\vec{\nabla}\vec{\nabla}\cdot(\vec{v} + \vec{J}_k) \right] \tag{103}$$

The right hand side vanishes except at the electrodes. In this geometry the "inertial" terms $\vec{\nabla}(\rho_\alpha \vec{v}\vec{v})$ are zero. (Even where they are not, the approximation of setting them equal to zero, corresponding to "creeping flow" in hydrodynamics, is certainly a good one here.)

Upon adding Eqs. (103) together we find that

$$\nabla^2(\vec{v} + \sum_k \eta_k\vec{J}_k/\eta) = 0$$

$$\sum_\alpha \eta_{\alpha k} = \eta_k \tag{104}$$

Since $\vec{v}$ and the $\vec{J}_k$ vanish at the cell walls by virtue of the assumption of laminar flow, it follows that

$$\vec{v} + \sum_k \eta_k\vec{J}_k/\eta = 0 \tag{105}$$

Eq. (105) expresses the local (mass average) velocity, $\vec{v}$, with respect to the cell walls in terms of the peculiar velocities and the partial viscosities.

In the most general case, the details of the sources and

sinks of the bounding surfaces and of the concentration changes accompanying the electrolysis must be taken into account to obtain detailed solutions to the equations of motion.

Transference numbers. We have previously found that the transference numbers in the reference frame of the local center of gravity are

$$t_i = z_i \mathcal{F} \vec{J}_i / \vec{I}$$

(80)

$$= z_i \mathcal{F} \sum_k L_{ik} / \sum_k z_i z_k L_{ik}$$

If, instead, the walls of the cell are taken as reference point then $\vec{J}_i$ is replaced by $\vec{j}_i + \vec{v}$ and

$$t_j = c_i z_i \mathcal{F} (\vec{J}_i + c_i \vec{v}) / \vec{I}$$

(106)

$$= t_i^o + \delta t_i$$

$$\delta t_i = c_i z_i \mathcal{F} \vec{v} / \vec{I}$$

Using Eq. (105) we find that

$$\delta t_i = c_i z_i \mathcal{F} \sum_k \eta_k \vec{J}_k / \vec{I}$$

and therefore that

$$\delta t_i = \sum_k \frac{c_i z_i}{c_k z_k} \frac{\eta_k}{\eta} t_k^o$$

(107)

In the one component case, for example, we find that

$$\delta t_i = t_2^o \cdot \eta_1 / \eta$$

$$t_1 = t_1^o + \delta t_1 = \eta_2 / \eta$$

(108)

Thus, the transference numbers in the center of gravity reference system in the approximation that viscous and inertial forces can be ignored, can be expressed in terms of the friction coefficients R_{ik} alone. However, the interaction with the walls causes the transference numbers in the frame of reference determined by the cell wall to differ from these by an additional term, δt_i, which is expressed in Eq. (108) as a function of the partial viscosities and of the t_i^o themselves.

Since viscous shear is written in terms of a tensor of the second rank and friction in terms of a polar vector (tensor of the first rank), there can be no interaction among them in the sense of the Onsager reciprocal relations among phenomenological coefficients (Curie's Law).

Diffusion coefficients. When velocity of the local center of gravity with respect to the walls of a cell given by Eq. (105) is inserted as $\vec{v}_{PM}$ into Eq. (78), we obtain

$$
\begin{aligned}
\vec{J}_i^{(P)} &= \vec{c}_i \, \vec{v}_{PM} + \vec{J}_i \\
&= \sum_k [\Lambda_{ik} - \rho_i/\rho_\eta \sum_s \eta_s \, \Lambda_{sk}] \, \vec{\nabla}_T \tilde{\mu}_k \\
&= \sum_k (\Lambda_{ik} + \delta\Lambda_{ik}) \, \vec{\nabla}_T \tilde{\mu}_k
\end{aligned}
$$

$$
\delta\Lambda_{ik} = - \rho_i/\rho_\eta \sum_s \eta_s \Lambda_{sk}
$$

(109)

The fundamental diffusion coefficients measured in this frame of reference do not in general conform to the reciprocal relations since

$$(\Omega_{ik} + \delta\Omega_{ik}) - (\Omega_{ki} + \delta\Omega_{ki}) = \delta\Omega_{ik} - \delta\Omega_{ki} \qquad (110)$$

and, in general,

$$\delta\Omega_{ik} = -\frac{\Gamma_i}{\Gamma\eta} \sum_s \eta_s \Omega_{sk} \neq -\frac{\Gamma}{\Gamma\eta} \sum_s \eta_s \Omega_{si} \qquad (111)$$
$$\delta\Omega_{ki}$$

The difficulties in removing the effect of the bulk flow in this frame of reference (sintered glass disc for example) suggest that it might well be avoided except for the purpose of studying the partial viscosities themselves by obtaining $\delta\Omega_{ik}$.

I. Thermoelectricity and Thermal Diffusion

When a temperature gradient is imposed across a multi-component system, a flow of matter is induced which continues until a steady state composition gradient is established (Sôret steady state). The quantity $\partial \ln c_k / \partial T = \sigma_k$ is the steady state Sôret coefficient. If an electrolytic system is fitted with a pair of electrodes reversible to one of the ionic species (Fig. 3), then the temperature gradient gives rise to a thermopotential. The initial value corresponding to uniform composition gradually changes as the thermal diffusion sets up a composition gradient, finally

stabilizing at the value characteristic of the Sôret steady state.
The thermopotential measured in electrolyte systems can be related
(vide infra) to the heat absorbed at one electrode and released at
the other electrode during isothermal electrolysis.

In order to examine these phenomena we return to the
phenomenological equations which include temperature gradients:

$$\vec{\nabla}_T \tilde{\mu}_i = - \sum_{k=1}^{n} R_{ik} \vec{J}_k - R_{i,n+1} \vec{\nabla} \ln T \qquad i = 1 \ldots n \qquad (112)$$

$$R_{ik} = R_{ki}$$

$$\sum_{k=1}^{n} R_{ik} = 0$$

$$\vec{J}_i = - \sum_{k} L_{ik} \vec{\nabla}_T \tilde{\mu}_k - L_{i,n+1} \vec{\nabla} \ln T \qquad i = 1 \ldots n+1$$

$$L_{ik} = L_{ki} \qquad (113)$$

$$\sum_{k=1}^{n} M_k L_{ik} = 0$$

We introduce the definition of the n quantities Q_k^*:

$$\sum_{k=1}^{n} L_{ik} Q_k^* = L_{i,n+1} \qquad (114)$$

so that we may write (113) in the form

$$\vec{J}_i = - \sum_{k=1}^{n} L_{ik} (\vec{\nabla}_T \tilde{\mu}_k + Q_k^* \vec{\nabla} \ln T) \tag{115}$$

Eq. (114) is not a complete definition of the Q_k^* since the L_{ik} are not independent, i.e. the L matrix is singular. The definition is completed below.

The reason for the choice of the form (114) may be seen by examining the dissipation function

$$
\begin{aligned}
\Phi &= - \sum_{k=1}^{n} \vec{J}_k \cdot (\vec{\nabla}_T \tilde{\mu}_k + Q_k^* \vec{\nabla} \ln T) \\
&= - \sum_{k=1}^{n} \vec{J}_k \cdot (\vec{\nabla}_T \tilde{\mu}_k) - \sum \vec{J}_k Q_k^* \vec{\nabla} \ln T) \\
&= - \sum_{k=1}^{n} \vec{J}_k \cdot (\vec{\nabla}_T \tilde{\mu}_k) - \vec{q} \cdot \vec{\nabla} \ln T)
\end{aligned}
\tag{116}
$$

The relation $q = \sum_k J_k Q_k^*$ is the basis for naming the Q_k^* "heats of transfer."

The independence of the dissipation function of a translation of the entire system with a uniform velocity can be expressed as $\sum_i c_i (\vec{\nabla}_T \tilde{\mu}_i + Q_k^* \vec{\nabla} \ln T) = 0$ in an unaccelerated system at uniform pressure. With the Gibbs-Duhem relation this leads to

$$\sum_{k=1}^{n} c_i Q_k^* = 0 \tag{117}$$

This relation combined with (114) constitutes a complete definition of the Q_k^*.

If a temperature gradient is maintained until a steady state is attained in which the matter fluxes vanish, the system is said to be in the Sôret steady state.

$$\vec{J}_i = 0 = \sum_k L_{ik}(\vec{\nabla}_T \tilde{\mu}_k + Q_k^* \vec{\nabla} \ln T) \tag{117a}$$

Despite the singularity in the L matrix (and the non-independence of the forces), it may be readily shown that when (117a) obtains (117) plus the Gibbs-Duhem equation it leads to the conclusion that

$$\vec{\nabla}_T \tilde{\mu}_k + Q_k^* \vec{\nabla} \ln T = 0 \qquad\qquad k=1...n \tag{117b}$$

By forming neutral combinations of the ionic species, for example $\gamma_A A + \gamma_B B$ and defining $Q_{AB}^* = \gamma_A Q_A^* + \gamma_B Q_B^*$ we can write (117b) in terms of the neutral components.

$$\vec{\nabla}_T \mu_{AB} + Q_{AB}^* \vec{\nabla} \ln T = 0 \qquad\qquad (AB) = 1...n-1 \tag{117c}$$

The n quantities Q_k^* are related through (117) but the (n-1) quantities Q_{AB}^* are independent. In a different notation which is widely used

$$Q_{k/}^* T = S^* = \text{(entropy of transport)}$$

$$\bar{\bar{S}}_k = S_k^* + S_k = \text{(transported entropy)}$$

where S_k is the ordinary (thermostatic) partial molal entropy based on third law calculation. For these quantities Eq. (117) takes the form

$$\sum_i c_i S_i^* = 0$$

(117d

$$\sum_i c_i \bar{\bar{S}}_i = S_{sp}. \quad \text{(net entropy per unit volume)}$$

In terms of the transported entropy and noting that $\vec{\nabla}_T \tilde{\mu}_k = \vec{\nabla}\tilde{\mu}_k + S_k \vec{\nabla} T$ we can write (117b) as

$$\vec{\nabla}\tilde{\mu}_k + \bar{\bar{S}}_k \vec{\nabla} T = 0$$

(117e

By taking n-1 neutral combinations we can express (117e) as

$$\vec{\nabla}(\nu_A \tilde{\mu}_A + \nu_B \tilde{\mu}_B) = \vec{\nabla}\mu_{AB} = - \bar{\bar{S}}_{AB} \vec{\nabla} T = - (\nu_A \bar{\bar{S}}_A + \nu_B \bar{\bar{S}}_B) \vec{\nabla} T$$

(117f

$$\vec{\nabla}_T \mu_{AB} = - (\bar{\bar{S}}_{AB} - S_{AB}) \vec{\nabla} T = - S^* \vec{\nabla} T$$

From an experimental point of view $\vec{\nabla}\mu_{AB}$ is not easily measured. Since the composition gradient ordinarily is measured and the activity coefficients can be obtained from isothermal measurements, the isothermal gradient in chemical potential under conditions of the same composition, etc. as occur in the thermocell is just what is usually obtained experimentally. The Sóret coefficient σ may be written

$$\sigma = - \frac{d \ln m}{dt} = \frac{\nu_A S_A^* + \nu_B S_B^*}{(\nu_A + \nu_B)RT(1 + \partial \ln \gamma_{\alpha\beta}/\partial \ln m)_T}$$

(117g

where the ion concentrations are conventionally written in molality units. Thermocells. This subject has been discussed by many authors including Holton (1953), Eastman (1928), Sundheim (1956) and Tyrrell (1961). The following is similar to that given by Agar (1959).

For an alternative formulation utilizing electrically neutral combinations of ions, see Schneebaum and Sundheim (1961).

An electrochemical cell with a temperature gradient across the liquid electrolyte is represented schematically in Fig. 3 . The copper terminals at temperature T_o are attached to the measuring potentiometer which determines the emf under zero current conditions. This potential difference is given as the difference in $-\tilde{\mu}_e(T_o,$Cu $/e$ between two terminals. In a metallic thermocouple (electrolyte absent) this quantity can be obtained by integrating (117e) around the circuit, obtaining

$$e(\vec{\nabla}\psi/\backslash T) = \overline{\overline{S}}_e(T_o,M_1) - \overline{\overline{S}}_e(T_o,M_2) \tag{117h}$$

All experimental measurements of $d\psi/dt$ or of the Peltier heat are made on pairs of substances and give the difference of $\overline{\overline{S}}_e$ in the two materials. However, it is possible to determine the Thomsen coefficient $X = T(\partial\overline{\overline{S}}_e/\partial T)$ by measuring the temperature distribution along a single substance in which an electrical current is flowing. By extension of the third law principle to entropies of transport, i.e. assuming that $\overline{\overline{S}}_e = 0$ at 0^oK, the integration of (X/T) from 0 to T leads to evaluation of $\overline{\overline{S}}_e(T,M)$ for each substance (Temkin and Khoroshin, 1952).

In the cell shown in Fig. 3 it is supposed that there may be an electrode reaction involving the electron e, the constituents of the solutions, A_i, and possibly materials A_r in phases other than the solutions. The overall reaction for transfer of one Faraday of charge may be written as

$$\sum_{i=0}^{n} \gamma_i A_i + \sum_r \nu_r A_r + e = 0 \tag{118}$$

where the stoichiometric coefficients γ_i are positive for reactants, negative for products and zero for substances not involved in the reaction. At equilibrium

$$\Delta F = 0 = \sum_{i=0}^{n} \gamma_i \tilde{\mu}_i + \sum_r \nu_r \mu_r + \tilde{\mu}_e (T_1,M_I) \tag{119}$$

We may then write

$$\tilde{\mu}_e (T_o, Cu)_I = \tilde{\mu}_e (T, M_I) + \int_{T_o}^{T} \bar{\bar{S}}_e (T, M_I) \, dT \qquad (120)$$

For a similar electrode connected to terminal II

$$\tilde{\mu}_e(T_o, Cu)_{II} = \tilde{\mu}_e (T_o, M_{II}) = \tilde{\mu}_e (T + dT, M_{II}) + \int_{T_o}^{T + dT} \bar{\bar{S}}_e(T, M_{II}) \, dT \qquad (121)$$

Subtracting (121) from (120), the observed potential difference is calculated to be

$$e \, d\psi = - d\tilde{\mu}_e(T_o, Cu) = \sum_{i=1}^{n} \nu_i \, d\tilde{\mu}_i + \sum_r \nu_r d\mu_r - \left[\bar{\bar{S}}_e(T, M_{II}) - \bar{\bar{S}}_e (T, M_I) \right] dT \qquad (12?$$

(The convention treats the emf as positive if the higher temperature electrode is positive.)

If the system has come to the Sôret steady state (122a) may be applied

$$e \, d\psi_{st} = - \left[\sum_i \nu_i \bar{\bar{S}}_i + \left(\bar{\bar{S}}_e (T, M_I) - \bar{\bar{S}}_e(T, M_{II}) \right) \right] dT + \sum_r \nu_r \, d\mu_r \qquad (122a)$$

For a pair of electrodes which differ only in temperature $d\mu_r = - \tilde{S}_r \, dT$

and the last equation may be written as

$$e\, d\psi_{St} = -\left[\sum_i \nu_i' \bar{\bar{S}}_i + \nu_r' \bar{S}_r' + \bar{\bar{S}}_e\, (M)\right] dt \tag{123}$$

When the Sôret equilibrium has not been established, (123) can be written in the form:

$$e\, d\psi = e\, d\psi_{St} + \sum_i \nu_i'\, (d\tilde{\mu}_i + \bar{\bar{S}}_i\, dT) \tag{124}$$

This may be transformed by applying the condition for zero current and the definition of the transference number

$$I = e\sum_i z_i j_i = 0$$

$$= e\sum_i z_i \sum_k L_{ik} X_k$$

$$= -e\sum_k \vec{\nabla}_T \tilde{\mu}_k \sum_i L_{ik}\, \frac{t_k}{z_k}$$

$$0 = -\sum_k \frac{t_k}{z_k}\, \vec{\nabla}_T \tilde{\mu}_k$$

Subtracting this expression from (124) and using $d\tilde{\mu}_i = d_T \mu_i \pm S_i dT + z_i e\, d\psi$

$$e\, d\psi = e\, d\psi_{St} + \sum_i (\nu_i' - t_i/z_i)(d_T \mu_i + S_i^* \, dT) \tag{125}$$

in which the unmeasurable term $d\psi$ has been removed. We may now form

electrically neutral combinations of the species of the sort *so that*
$\gamma_i \mu_i + \gamma_j \mu_j = \mu_{ij}$.　**Eq. (125)**　describes the instantaneous
potential as an initial potential:

$$ed\psi = ed\psi_{st} - \sum_i \frac{t_i}{z_i} S_i^* \, d\eta$$

which is progressively modified by a diffusion potential $\sum_i \gamma_i' \, d_T \tilde{\mu_i}$
until the Sôret steady state is reached when $d\psi = d\psi_{st}$.

The Peltier heat, Π, which is the heat extracted from
one electrode and released at the other during an isothermal electro-
lysis, may be expressed by constructing an entropy balance at one
electrode

$$\Pi = \sum_i J_i Q_i^* + Q_{el}^* - T(\sum_i \gamma_i' S_i + \sum_r \gamma_r' S_r + S_e(T,M)) \tag{126}$$

It is easily seen that this implies that

$$e(d\psi/dT)_{initial} = \Pi/e \tag{17}$$

II. Experimental Methods

The determination of the various phenomenological coefficients as functions of temperature and composition for fused salt systems is not different in principle from that for other liquids. Nevertheless, some special problems arise from the absence of a well defined solvent, from the high temperatures and, in some cases, from the magnitude of some of the coefficients. In this section a brief account of methods which have been found useful is given. For details of the careful and frequently difficult measurements, the reader is referred to the original papers. A selection of data is given in Tables II-VII

A. Viscosity

The principal methods establish a stationary state of shear and determine the proportionality constant between the rate of shear and the force required to maintain it. MacKenzie (1958) has surveyed a number of experimental methods suitable for fused salts, slags and molten metals.

Poiseuille's Law applied to the Ostwald viscometer was used by Goodwin and Mailey (1907). In this type of instrument the small kinetic energy connections are required to allow for the term in grad $\rho v^2/2$, which was dropped from the convective derivative In the Ubbelohde-Bingham modification as used, for example, by Bloom et al. (1958), the experimental design makes such corrections unnecessary.

Another experimental arrangement rotates two concentric cylinders with respect to each other so that the liquid in the annulus is maintained in a state of shear. The torque required to maintain a constant relative angular velocity is a measure of the viscosity. This

method is particularly suitable for liquids of high viscosity, such as glasses and slags. In one modification Bockris and Lowe (1953) rotated the container and measured the torque on an inner spindle by balancing it against the torque produced by an electromagnet in the field of a permanent magnet.

The damping of the torsional oscillations of a disc produces a logarithmic decrement in the oscillations which is an index of the viscosity. An oscillating disc was employed by Lorenz and Hochberg (1916) and an oscillating sphere by Dantuma (1928) and by Jaeger (1930). The logarithmic decrement of the rotating crucible containing the melt has been used by Vetyukov et al. (1960) and by Janz and MacIntyre (1962).

A variation on the falling body methods based on Stoke's Law was employed by MacKenzie (1957) in which the falling sphere was partially counterbalanced.

Schematic diagrams of the various methods are shown in Fig. 4. MacKenzie (1959) recommends the capillary method described by Bloom et al. for fused salts of moderate viscosity.

The viscosity of most fused salts falls in the range 0.5 to 5 centipoise. Some representative values are given in Table II.

Some attention has been given to the change in density that accompanies increasing temperature at constant pressure. Jobling and Lawrence (1951) have remarked that the energy of activation at constant volume rather than at constant pressure should be employed to avoid spurious volume effects. (See also Collins, 1957).

MacKenzie (1958) points out that viscous flow is a passage

from one equilibrium position to another in the preferred direction of an applied stress. This movement requires that positions, i.e. "holes" be available in the liquid structure. The total activation energy may then be considered as consisting of two parts:

1. the energy required for establishing the hole and
2. the energy required for the moving unit to move into the hole.

If the total volume of the liquid is kept constant then the amount of free volume may be thought of as remaining approximately constant as well. Therefore, the energy of activation at constant volume is only that which is required for the moving units to move into this fixed amount of free volume. MacKenzie has collected together the available data on energy of activation for viscous flow at constant volume. He has further remarked that in these cases the ratio of the energy of activation at constant volume is only a small fraction of the energy of activation at constant pressure, being 0.2-0.5 for a number of unassociated liquids and 0.7-1.0 for a number of associated ones.

Bulk viscosity: This occurs in radial flow from a source and involves changes in the shape of a volume element as it moves outward along a sector. One method for measuring the coefficient of bulk viscosity is based on the determination of ultrasonic absorption. The coefficient of absorption of ultrasonic energy, α, is expressed (see Herzfeld and Litovitz, 1959) as

$$\alpha = \frac{2\pi^2 f^2}{c^3 \rho} (4/3 \eta + \theta) \qquad (128)$$

provided that there is a rapid exchange of energy between external and internal degrees of freedom. (Here f is the frequency, and c is the velocity of the sound waves, η is the coefficient of shear viscosity and ϑ the coefficient of bulk viscosity.) In most fused salts, there is reason to believe that this condition is satisfied. Higgs and Litovitz (1960) have determined the ultrasonic absorption and dispersion in several fused salt systems (Table III). They interpret these fresults as follows: they conclude that Eq. (128) is probably valid for simple fused salts and that ϑ is more sensitive to variations in structure than is η. They view their results as showing that the bulk viscosity is in some way related to the entropy of fusion, suggesting that some type of further lattice melting is required for the lattice rearrangements which occur in the structural relaxation process of both ionic and organic liquids.

B. Electrical Conductivity

The specific electrical conductivity of most fused salt systems is of the order of 1 $ohm^{-1}cm^{-1}$. In order to achieve accuracies of the order of a few tenths of a percent with conventional conductance bridges, cell constants of a few hundred cm^{-1} are required. For this purpose, capillary type cells are generally used. Representative designs are shown in Fig. 5. Pyrex or quartz bodies with platinum or molybdenum electrodes are usually employed although other materials have been used for very corrosive melts (e.g. Bajesy, 1962). Concentric metal spheres or cylinders have been employed although with some loss in accuracy. Because the temperature coefficients tend to be a few tenth of a percent per degree, the cell and its contents must be held at a temperature

uniform at least to a few tenths of a degree over the cell and also measured to the same accuracy. Since equivalent conductances are usually sought, measurements of density over the same temperature range and to the same accuracy are required.

Alternating current Wheatstone Bridges are ordinarily used. No frequency effect has been detected aside from that due to electrode capacitance and lead reactance. Plotting the apparent resistance against the reciprocal of the square root of the frequency and extrapolating to infinite frequency is usually considered adequate to eliminate these effects. However, see Hills (1962). No significant polarization effects at the electrodes have been encountered.

Oxides, borates, silicates, etc. often display conductivities of the order of several hundred cm^{-1} requiring cells of other types. A four terminal cell in which the DC current and potential drop in the cell are simultaneously measured is sometimes used for these systems.

Details of recommended experimental procedures may be found in papers by Van Artsdalen et al. (1955), Tomlinson (1959) and Bronstein (1962).

It has become common practice to compute an apparent activation energy for electrical migration from the slope of a graph of the logarithm of equivalent conductance versus the reciprocal of the absolute temperature. Attempts are frequently made to relate the apparent activation energy obtained in this way to energy and entropy changes of postulated unimolecular rate processes. However, such a procedure overlooks the important fact that the density of the salt changes with temperature, so that the spacing and hence the

energetics of any proposed mechanism must change with the temperature. That is, the dependence of the equivalent conductance on changes of temperature carried out at constant pressure may be viewed as the sum of the change due to the change in temperature at constant volume plus that due to the change in volume with temperature. The usual discussions of the effect of temprature on conductance ignore the second term. Direct measurements of this quantity are not available. However, the compressibilities characteristic of liquids suggest that profound energetic changes are probably associated with volume changes. Consequently, activation energies and similar quantities derived from the temperature coefficient of electrical conductance should be viewed with skepticism. Of course, the fitting of data to an approximate equation of this form provides a convenient means for rough extrapolations with a two parameter equation. Representative experimental results are given in Table IV.

C. Current Efficiency

The transport of electricity by the migration of ions is associated with chemical changes at the electrodes (the terms involving the divergences in Eq. (11). The amount of chemical change produced at an electrode divided by the change expected on the basis of the postulated electrode mechanism is called the current efficiency of that electrode. Thus, Faraday's Law states that the current efficiency of an ionic conductor is 100%. Deviations from such efficiencies may come about for two reasons. In the first place, the electrode reaction may be incorrectly identified. In the second place, there may be a mechanism of electrical conductivity which does not entail material transformations at the electrodes, i.e. electronic conductivity, as in the case of metal. A further

complication sometimes is encountered in fused salt systems. The
electrode products may be soluble in the salt, e.g. sodium in molten
sodium chloride. Since the material produced at the cathode dissolves
in the melt, it is difficult to be sure about the amount produced by
the electrode reaction.

The relative probabilities of electronic vs. ionic charge
transfer through the liquid should be viewed as being essentially
distinct from the relative probabilities of electronic vs. ionic
charge transfer across the boundary from the liquid to the electrode.
Electrodeless conductance measurements, e.g. with inductive coupling,
such as employed by Yosim et al. (1962), should make it easier to
separate the two steps.

In any event, experimental measurements of current efficiencies
have led to the following results: All fused salts that have been
studied thus far have displayed close adherence to Faraday's Law
except for Sb_2S_3, Cu_2S and Cu_2S/FeS and FeO/SiO_2 where the current
efficiencies indicate that ionic and electronic conductivity (possible
p type semiconduction) occur simultaneously. It has been suggested that
a small amount of electronic conductivity occurs in all molten salts
as in all solids, but that only in very poor conductors in which the
electronic component is particularly high is it possible to detect
its presence. No results have been reported to date on the very
interesting metal-molten salt solutions.

D. Determination of Transport Numbers in Fused Salts

The complete definition of the transport (or transference) numbers of the ionic constituents of a fused salt system requires the identification of the reference point used for the ionic velocities. Two early studies are of interest: Lehrman (1885) observed the migration with respect to the glass slide of crystals of silver, of bubbles and of crystals of silver iodide in molten silver iodide undergoing electrolysis under a microscope between Pt electrodes. He noted that all of these migrated in the same direction as positive electricity. Lorenz and Fausti (1904) carried out a series of Hittorf type experimental tests through porcelain membranes for solution of $PbCl_2$ in KCl and NaCl with poor results. Warburg (1884) determined transference numbers of ions in glass and quartz by visual determination of the extent of penetration by the ion and concluded that only the cations were mobile. A summary of a number of early, but inconclusive experiments is given by Lorenz (1905).

The design of modern experiments is to a considerable extent concerned with preventing gravitational forces from causing a "flowback" which tends to obscure any movement of the salt. That is, in the simplified experimental design pictured in Fig. 6, flow of electricity causes a movement of the salt with respect to the electrodes if no further precautions are taken. However, gravity causes the liquid levels in the two arms to remain equal. Most transference number experiments introduce a membrane of some sort between the arms of the cell to minimize the effect. The selection

of the membrane material is a compromise between sufficiently low

electrical resistance and sufficiently high hydrostatic resistance.

Aluminum oxide, Pyrex, quartz, asbestos, corundum, boron nitride,

etc. have been used for this purpose. The motion is detected by direct

weight change on each constituent [Karpachev and Pal'guev

(1949), Delimarskii et al. (1955), Sundheim and Harrington (1957),

Kellogg and Duby (1963)], motion of an indicator bubble [Duke and

Laity, (1955)] or of the bounding surface of the system [Bloom and

Foull (1955), Lorenz and Janz (1957)] . A moving boundary method

[Duke and Crook (1958)] may be employed if following salts of appro-

priate density can be found. Radiotracers may be used to follow motion

of the salt across the membrane [Wirtz (1957), Frank and Foster (1957),

Duke and Fleming (1958)]. An ingenious method has been proposed

by Klemm (1960) in which the steady state of simultaneous trans-

ference and gravitational flow are balanced. By determining the

hydrodynamic and electrical resistivity separately, the electro-

migration may be identified.

For mixtures any of the above methods can be used coupled

with determination of concentration changes [Duke and Fleming (1959),

Laity (1957)]. In addition, the emf of various cells with trans-

ference (see below) may be used to give information.

A summary of experimental results is given in Table V.

At present the reliability of any set of measurements as estimated

for its reproducibility and comparison with results found by other

methods is rarely better than about 15%.

E. Diffusion

        The methods of determination of diffusion coefficients in
fused salt systems differ from those suitable for low temperature
systems only with respect to the precautions that are often necessary
because of the corrosive nature of some melts, because of the volume
changes upon melting and freezing and because of the greater difficulty
in avoiding convection due to temperature gradients. To date few
interdiffusion coefficients have been determined; most studies have
been restricted to self-diffusion coefficients.

        Yang and Simnad (1959) have surveyed some of the principal
experimental techniques. A diffusion couple method has been employed
by Towers, Paris and Chipman (1953) and by Towers and Chipman (1957)
to study self-diffusion of Ca and Si in slags. In one set of experi-
ments a column of molten slag containing the radioactive tracer was
brought into contact with a second column of unlabeled material.
After a fixed time the system was quenched and the distribution of
radioactivity in the solid rod determined. Volume changes accompanying
the freezing process make this unsuitable except for approximate
measurements unless the volume changes are known to be very small.

        A significant improvement is afforded by the "vacuum
bubble" technique of Angell and Bockris (1958) and by Bockris and
Angell (1959). The two columns are brought into contact by collapsing
a small gas bubble which separates them initially. At the end of the
fixed time the columns are separated by breaking the containing tube
at the same distance from the closed end of the tube as the initial
bubble was collapsed. The two separate halves may then be removed
for analysis without modifying the distribution of tracer between

the two halves by volume changes upon freezing.

The method of Anderson and Saddington (1949) in which the labeled material is allowed to diffuse from a capillary closed at one end into a bath of unlabeled material has been adopted to fused $NaNO_3$ (both ions) by Van Artsdalen et al. (1956) and by Borucka et al. (1957) for fused NaCl. Djordjevic and Hills (1960) made use of diffusion out of a porous disc to determine the self diffusion coefficient in molten Na_2CO_3.

Measurements of interdiffusion have been made by McCallum and Barret (1952) who measured the concentration variations in a molten silicate diffusion couple by freezing the couple and determining the gradient in the resulting glass. Interdiffusion coefficients where one species is quite dilute are readily measured by chrono-potentiometry. The relevant theory and techniques are discussed in Chapter IV. Table VI summarizes the data on tracer diffusion and and Table VII that on interdiffusion. Fig. 7 shows some experimental designs.

F. Experimental Methods for Thermoelectric Measurements

For one component fused salts, measurements of the thermo-electric power can be readily carried out, e.g. Sundheim and Rosenstreich (1956), Nichols and Langford (1960) by some sort of differential heating arrangement (Fig. 8). The transported entropy of the electron $\bar{\bar{S}}_e(T,M)$ has been estimated by integration from $0°$ to T of the Thomsen heat divided by the temperature. The Thomsen heat is obtained by combining experiment, extrapolation and the assumption that $\bar{\bar{S}}_e = 0$ at $T = 0$ and in any superconducting metal. The value estimated for $\bar{\bar{S}}_e(500°K,Ag)$ is .05 cal/deg/mole and hence may be

ignored in the present application. Then the third law entropy of the electrode material may be combined with the experimental thermoelectric power to obtain $\bar{S}_i$ for the ion to which the electrode is reversible ($= \bar{S}_2 \, z_1/z_2$). The available data are summarized in Table VIII.

The only thermoelectric measurements reported thus far on multicomponent systems is the report on the initial thermoelectric power of the $AgNO_3/NaNO_3$ system as a function of composition (Schneebaum and Sundheim, 1961) and the observations of approximate Sŏret coefficients by Nagoura and Sasaki (1956).

A technique for the determination of the thermoelectric power in the Sŏret steady state has been devised (Kellner and Sundheim, 1962) in which the effects of convection are minimized by holding the salt within a porous plug. One side of the plug is closed by an electrode held at one temperature; the other is in contact with a stirred liquid reservoir held at a second temperature. The evolution of the emf can be followed as a function of time and the final composition gradient determined by quickly making the temperature uniform and measuring the diffusion potential.

Direct measurements of the Peltier heat in fused salts are feasible but have not been reported as yet. Thermal conductivity data is very limited. As a rough estimate, the values for many salts are of the order of that for liquid water at room temperature.

III. Discussion

A sound theory of transport processes in liquids is scarcely feasible at present in view of the rudimentary nature of extant theories of the equilibrium properties of liquids. Fused salts offer further difficulties over simple liquids since there are at least two different species and long range as well as short range forces to deal with. Thus the time is far from ripe for a priori quantitative theories. Rather, we must content ourselves with a comparison of fused salts with simple liquids and with comparisons of the properties of one fused salt system with another.

A. Fundamental Theories of Liquids

The transport processes with which we have been concerned here are all irreversible in nature. In view of the time reversibility of both the classical and quantum mechanics, one must conclude that the phenomenological, macroscopic irreversibility must be statistical in nature. In general one considers systems which are only slightly removed from equilibrium and studies the rate of return to the equilibrium state. The properties of a one component fluid are described sufficiently for many purposes by giving two distribution functions, i.e., the pair distribution function n_2 which gives the probability of simultaneously finding particles in two given volume elements and the velocity distribution function f which gives the probability that a molecule has a velocity in a given range,(e.g. Green,1960).

For example, diffusion can be described beginning with the calculation of the relative velocity of two molecules

$$u_a - u_b = \int (f_a/n_a)\, \vec{v}_a\, d\vec{v}_a - \int (f_b/n_b)\vec{v}_b\, d\vec{v}_b = -D\nabla(n_a/n_b) \tag{129}$$

The calculation of f as a function of position and initial conditions would be sufficient to allow computation of the thermal and self-diffusion coefficients. The microscopic structure of the fluid enters indirectly into this expression in that the evaluation in terms of the local distribution depends upon the fact that the mean free path of a molecule is so very short that the distribution of relative molecular velocities is strongly dependent upon the relative positions in the liquid. With the aid of Liouville's theorem, a set of differential equations can be written for the distribution functions of substances of h of the N molecules. As Collins and Raffel remark, "There is no requirement implicit in this equation which assures that the average forces acting will lead to a drift of the system toward thermal equilibrium instead of away from it and no progress has been made in solving it in the absence of additional assumptions."

One method of proceeding which was developed by Kirkwood (1946) is based on extension of the concept of Brownian motion to molecules. That is, the average forces felt by a group of molecules due to their introduction with the remaining molecules is similar to the average frictional force which is proportional to the peculiar velocity (velocity with respect to the local center of gravity). By a process of averaging, it is shown that the particle carries out a random walk in velocity space just as in physical space. The Fokker-Planck equation obtained in this way is a time-irreversible equation for the distribution function. A characteristic quantity appearing in this theory is the friction coefficient ξ. Kirkwood devised an explicit but rather intractable formula for ξ on the

basis of molecular theory. The various transport coefficients may
then be expressed in terms of the friction coefficient and various
integrals over the pair potential.

A different fundamental approach is adopted in the fluctuation
dissipation theory (Kubo, 1957). Here the response of the system to
an external force is treated by a perturbation method. The transport
coefficients are expressed in terms of the fluctuations in the dynamical
fluxes at equilibrium. Time irreversibility enters this theory by the
omission of higher terms in some of the expansions.

A number of other studies have been made which proceed
from some sort of modification of the Maxwell-Boltzmann equation.
Reviews of theories of transport properties include those by Rice and
Frisch (1960), Collins and Raffel (1958) and Green (1960).

A recent discussion specifically concerned with transport
in ionic melts is given by Rice (196/). The system is taken to be a
so-called ideal ionic melt which consists of oppositely charged ions of
equal size and with identical internal properties (except for the sign
of the charge). For this system the problem under consideration reduces
to an equivalent one component system. In view of the high energy
of configurations which bring ions of the same charge close
together, it is assumed that hard core encounters between like ions
may be neglected. The development is based on a theory of Rice and
Allnatt (1961) for the singlet and doublet distribution functions.
The essential dynamical event is taken to be a hard core collision
of a pair of ions followed by a quasi-Brownian motion under the influence
of the fluctuating field of the neighboring ions. By a series of

plausible but unproven assumptions, it is concluded that only the short range forces are important in transport processes, so that viscosity, self-diffusion and thermal conductivity of liquid KCl, for example, may be compared with those of liquid argon (Ar is isoelectronic with K^+ and Cl^-). Moderately good agreement with experiment is reported.

In other words, the transport properties of fused salts (except for those related to electrical conductance) like many other properties of these systems show very little difference from those of liquids which do not involve long range Coulombic forces. (The long range and relatively great strength of this Coulombic potential lead to large cohesive energy densities of fused salts but affect few other properties.)

Yet another method of dealing with the statistical mechanical derivation of transport makes use of perturbations to the equilibrium distribution functions (see Bearman, 1961). The expression for the mean friction force experienced by a molecule of shear in a system of j components undergoing one-dimensional isobaric isothermal diffusion is

$$\overline{F}^{(1,1)*} = 1/2 \sum_{\beta=1}^{j} c_\beta (\vec{r}/r)(dV_{\alpha\beta}/dr)(q_{\alpha\beta}^{(2,1)} - g_{\beta\alpha}^{(2,1)}d^3\vec{r}$$

Here c_β is the concentration of species β. The potential of intermolecular force, $V_{\alpha\beta}$, depends only on the intermolecular distance r; effects of orientation and internal degrees of freedom, if present, are assumed to have been averaged out. The equilibrium radial

distribution $g_{\alpha\beta}^{(2,0)} = \exp(-W_{\alpha,\beta}/kT)$ where $W_{\alpha\beta}$ is the potential of mean force acting on a molecule of species α near a molecule of species β. The quantity $g^{(2,1)}$ is the difference between the non-equilibrium pair distribution function and the equilibrium radial distribution function. If this perturbation is expanded in a plausible form and treated as a linear function of the velocities, transport expressions can be obtained which have the form of the phenomenological equations.

After the coefficients are identified by comparison with the phenomenological equations, the transport properties are expressible in terms of the perturbations. These in turn must be obtained by molecular theories. A significant simplification is afforded by assuming that the radial distribution functions are independent of composition at constant temperature and pressure and that the volumes are additive. Then particularly simple expressions for some of the transport quantities are obtained.

At a less fundamental level two other approaches to transport in liquids are widely used. The hydrodynamic model pictures a moving molecule like a particle moving through a fluid which offers frictional resistance to the flow. Thus a mobility is assigned to each particle on the basis of Stoke's law, so that the response to various external forces can be immediately written down.

The Eyring transition state theory has been applied to liquid systems by Eyring and his collaborators. In its original form (e.g. Glasstone, Laidler and Eyring, 1941), it is based on a quasi-crystalline model of the liquid. The elementary step is taken to be a jump into a vacant position. The rate of such jumps is

discussed in terms of the activation energy required to overcome the potential energy barrier found by the surrounding species and the rate at which such a barrier can be crossed (an interesting critique of this model and its relation to the statistical mechanical formulations has recently been given (Bearman, 1961)). In order to extend this model to fused salts we note that the quasi-crystalline structure implied by the model is particularly appropriate. However, the low probability of finding a cation vacancy adjacent to a cation implies either that the activation energy will be high and the jump frequency low or that the elementary step involves the cooperative adjustment of a number of ions. This sort of formulation has been explored by Rice (1958) for solids. Recently, the "significant structures" theory (Eyring, et al., 1958) has been proposed. Here the crystal-like regions are imagined to be intermixed with gas-like regions. The effective perturbation function is obtained by a judicious mixture of these two extremes. It seems likely that the introduction of a further parameter (the relative proportion of the two types) will improve the results. The important drawbacks of this theory are its ad hoc character and the difficulty of clearly assessing the nature of the approximations involved.

B. Principle of Corresponding States

In order to use any of these rather general theories in discussing the properties of molten salts, it is important to decide under what circumstances the properties of different salts should be compared. That is , is there a law of corresponding states for the transport properties of molten salts?

It is interesting to note that very different liquids sometimes may have similar transport properties. Apparently, the nature of the molecular intereactions does not, per se, permit prediction of the viscosity, for example.

Dimensional considerations (Hirschfelder, et al., 1954) and analysis of the molecular basis of the transport properties (Rice and Frisch, 1960) have been used to prove that simple liquids, i.e. those composed of spherical molecules interacting with two parameter potential energy functions, do in fact possess transport properties which are functions only of the reduced temperature and volume. It is possible to extend the dimensional argument to polar molecules (Rowlinson and Townley, 1953) and to elliptical ones.

In order to consider the possibility of there being a reduced equation of state and reduced transport parameters for molten salts, we examine the form of the potential energy function. The simplest model which might reasonable be expected to reproduce the principal features of a simple molten salt consists of two sets of hard spheres of radius r_1 and r_2 respectively and bearing the charges z_1e and z_2e. In this approximation the short range dispersion forces, polarizability, etc. are ignored and the total potential is taken to be the sum of pair potentials.

$$\mathcal{U} = \sum_{i>k} u_{ik}(r_{ik})$$

$$u_{12}(r_{12}) = u_{12}(r_{1},r_{2},z_{1},z_{2},r_{12})$$

The thermodynamic and transport quantities will be functions of the variables r_1,r_2,z_1,z_2,m_1,m_2 and kT. These may be written in dimensionless groups as $r_1/r_2, r_1/V^{(1/3)}, m_1/m_2, z_1/z_2, z_1z_2e^2/(r_1 + r_2)kT$ which may be used to define a reduced volume, $V/r_1^3 = V^x$ and a reduced temperature, $T^x = T(r_1 + r_2)k/(z_1z_2e^2)$. Two salts characterized by the same values of $r_1/r_2, z_1/z_2$ and m_1/m_2 would have the same thermodynamic and transport values at the same reduced volume and temperature. However, just about all data available are taken at constant **pressure, so** that it is generally not possible to find data at corresponding states. It would be helpful if experimenters would give more attention to constant volume measurements.

The melting point (approximately the triple point) may be used as a corresponding temperature. Selecting the alkali halides with nearly the same values of $r_1/r_2, z_1/z_2, m_1/m_2$ (from crystallographic radii) we find that their reduced melting points and reduced densities at the melting point compare fairly well.

A reduced equation of state for ionic salt has been obtained recently by Reiss, Mayer and Katz (1961) by an approximate analysis of the configuration integral. They have noted that the close approach to each other of ions of like charge is very unlikely, separation by an ion of opposite charge being the practical closest approach. Here the centers of the like cores are separated by $2(r_a + r_b)$. Naturally

the closest approach of ions of opposite charge is $(r_a + r_b)$. If the system may be treated as a set of hard spheres on which the Coulombic potential is superimposed, then the potential energy function for the system can be characterized by a single distance scale factor, namely $r_a + r_b = r$. With this simplification, the equation of state of a symmetrical salt of valence z may be obtained in terms of the reduced variables:

$$\pi = \pi(\tau, \sigma)$$

$$\pi = r^4 \rho / z \qquad = \text{reduced pressure}$$

$$\tau = r r T / z \qquad = \text{reduced temperature}$$

$$\sigma = v/r^3 \qquad = \text{reduced volume}$$

For example, the authors calculate that the melting point of many symmetrical salts is given by

$$T_m = z/r(3.19 \times 10^{-5})^\circ K$$

The rough success of this theory (Table IX) provides a basis for selecting corresponding conditions to compare transport properties of different salts, since we expect that a similar rough corresponding state theorem will hold for transport properties.

Some interesting conclusions of a general nature have been drawn by Rice (1962) by examination of relaxation behavior of a simplified ionic melt. For simplicity, the fused salt is considered to be composed of oppositely charged ions of equal size and charge and with identical electronic proportions (except for the sign of the charge). For this system the problem under consideration reduces

to an equivalent one species system. The equilibrium properties of this
ideal ionic fluid have been examined by Rice and Allnatt (1961) who
have obtained approximate expressions for the equilibrium singlet
and doublet distribution functions.

The same authors consider the transport properties as well.

The separation of force fields into short range (hard core) and long
range (Coulombic) potentials leads to a transport equation containing
both Boltzmann and Fokker-Planck types of terms. A plausible but
non-rigorous argument leads to the conclusion that only the short
range forces make significant contributions to the friction coefficient.
In fact, the transport coefficients can be reasonably well correlated
with those of inert gases. Thus, K^+, Cl^- and Ar are isoelectronic
so that we find liquid KCl and liquid Ar may be expected to resemble
each other at corresponding densities. **The tracer diffusion
coefficient of argon at its melting point is found**
to be 2.07×10^{-5} cm^2/sec at $84.6^{\circ}K$ (Corbett and Wang, 1956), which
is certainly within the general range expected for the self-diffusion
coefficients of KCl near its melting point.

Similar conclusions were drawn with respect to the thermal
conductivity and viscosity.

A form of a law of corresponding states for transport
properties of simple fluids can be derived in several ways from
transport theories (cf. e.g., Rice and Frisch, 1960). For a one
component liquid the result is that if the potential $U(R)$ takes
the form

$$\mathcal{U} = \mathcal{E}\,\mathcal{U}^*(R/\sigma), \quad \text{then}$$

$$D^* = D_m^{1/2}/\mathcal{E}^{1/2}\sigma$$

$$\eta^* = \eta\sigma^2/\sqrt{m\mathcal{E}}$$

$$\varphi^* = \varphi^2/\sqrt{m\mathcal{E}}$$

$$\kappa^* = \kappa R\,\mathcal{E}^{1/2}/m^{1/2}\sigma^2$$

Each of the reduced quantities is a universal function of the reduced temperature and pressure (or volume).

$$T^* = kT/\mathcal{E}\quad;\quad V^* = V/\sigma^3;\quad p^* = p\sigma^3/\mathcal{E}$$

The theory is expected to be only very approximate since the coefficients seem to be quite sensitive to the details of the potential energy function.

C. Phenomenological Coefficients

If we pass from the mechanistic description at the molecular level to a non-specific macroscopic description, we are led to the linear phenomenological equations. Their formulation, as described in the beginning of this chapter, may be viewed as follows: The relation between the forces and fluxes is certainly valid only for not too large departures from equilibrium. For example, at high electric fields Ohm's law will no longer be obeyed, for a high enough temperature or composition gradients local thermodynamic functions may not even be definable; for chemical reactions the linear law is frequently not even approximately followed. Thus it is important to determine the domain of applicability of the linear approximation.

Except for studies of the Wien effect, systematic experimental examination of this question has not been carried out. Departures from the linear laws ordinarily are represented in terms of the non-constancy of the transport coefficients as functions of the parameters of the system. Provided that these variations are not too large, it is certainly more convenient to retain the linear expression by this means.

With regard to the Onsager reciprocal relations, two points of view may be taken. On the one hand the theoretical foundations may be thought to be unquestionably sound and experimental verification is then either redundant or, in fact, tests the experimental method. On the other hand, it may be held that empirical examination is required. This matter has been examined by Miller (1960), who has concluded that the available data support the view that the Onsager relations correctly describe the observed situation within the limits of experimental error for a wide variety of systems.

Accepting the validity of linear formulation and of the reciprocal relations, we must then enquire as to the nature of the conclusions that can be drawn from experimentally determined values of transport coefficients. It is clear that no deductions can be drawn about either structure or mechanism of transport without the use of a model. This point would seem to be too well understood to belabor it. However, the nature of the model being employed has often not been made explicitly with the unfortunate consequence of carrying into one field from another relations and concepts whose applicability has not been carefully examined. Thus the concept

of a well defined jump from a site to a vacancy as constituting the elementary step in diffusion arose in the study of crystals. Its utility in fused salt systems, for example, is to be determined on its own merits and not simply assumed. Similarly, partial ionic conductances and their relation to diffusion coefficients have been discussed in terms of specific models for various solids and solutions. On passing to a new system such as a one component fused salt the operational meanings of the quantities involved need to be examined and compared with the properties of various models.

It is strongly recommended that scientists writing on these topics take special pains to identify clearly their basic assumptions.

Table I. Relations between Phenomenological Coefficients

$$R_{ik}$$

$$r_{ik} \xleftrightarrow{\ (30)\ } R_{ik} \xleftrightarrow{\ (50)\ } R_{ij,kl}$$

$$\uparrow (26a)$$

$$(24)$$

$$R_{ik}^{(n)} \qquad L_{ik}$$

$$\updownarrow \qquad \updownarrow (33,66)$$

$$D_{ik}^{o} \xleftrightarrow[\ (68)\ ]{\ (70)\ } L_{ik}^{o}$$

$$(74) \uparrow (75) \qquad \uparrow (78)$$

$$D_{ik}^{V} \qquad L_{ik}^{P}$$
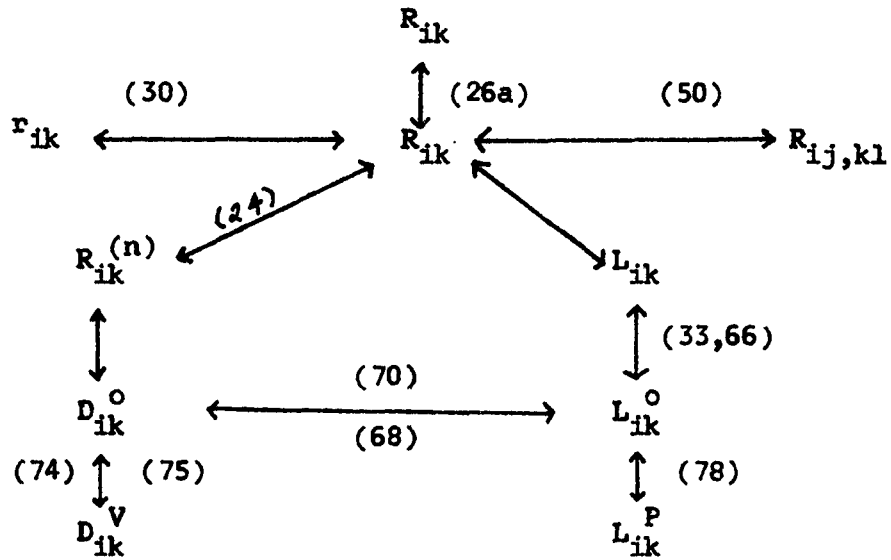
The figures in parentheses refer to pertinent equations in the text.

Table II. Viscosity

Salt	η (poises)	T (°C)	$E_{visc.}$ (Kcal/mole)
NaCl			9.1
NaBr			8.0
KCl			7.4
KBr			8.0
PbCl$_2$	2.22	650	6.7
PbBr$_2$	3.73	500	6.2
CdCl$_2$	2.03	650	4.0
AgCl	2.08	500	2.9
AgBr	2.83	500	3.1

References:

B. Harrap and Haymann (1950)

Dantuma (1928)

Table III. Bulk Viscosity

Salt	η-Centipoise	$T\,^{\circ}C$
$LiNO_3$	9.89	262
	7.95	300
	4.81	379
$NaNO_3$	11.3	310
	8.2	350
	6.9	449
$AgNO_3$	24.4	213.5
	19.9	251
	15.0	327
KNO_3	27.0	336
	21.6	393
	20.7	439
$CdCl_2$	4.4	574
	3.8	613
	3.3	650
$X\ NaNO_3/1-X\ KNO_3$		
$X = 0.2$	19.5	302
	15.4	375
$X = 0.5$	15.0	280
	9.9	373
$X = 0.8$	11.1	276
	8.2	396

Reference: Higgs and Litovitz (1960)

Table IV. Conductivity Data

Substance	Temp. Range	Conductivity $\lambda = a + bt^2 - ct^2\ \Omega^{-1}cm^{-1}$			Remarks	Ref.
		a	$b \cdot 10^2$	$c \cdot 10^6$		
LiCl	630-790°C	+0.5282	1.125	4.554		1
LiBr	555-750	+1.0095	0.7834	2.057		
LiI	475-670	-0.578	1.348	9.695		
NaCl	810-1030	-0.1697	0.6259	1.953		
NaBr	750-960	-0.4392	0.5632	1.572		
NaI	675-915	-0.8202	0.5940	1.976		
KCl	790-930	-1.7491	0.738	3.000		
KBr	737-960	-3.2261	1.0124	4.828		
KI	720-920	-1.7100	0.6408	2.965		
RbCl	730-935	-1.8097	0.6176	2.1985		
RbBr	700-905	-3.0505	0.9104	4.510		
RbI	655-885	-1.0798	0.4055	1.6305		
CsCl	650-900	-1.8023	0.5628	1.765		
CsBr	644-860	-1.4137	0.4255	1.228		
CsI	640-865	-1.3313	0.3958	1.305		

$$\lambda\ in\ \Omega^{-1}cm^{-1}$$

$MgCl_2$	720-960	1.165 + 0.00195(t-800)	2
$CaCl_2$	760-960	1.96 + 0.0035(t-800)	
$BaCl_2$	760-1080	1.440 + 0.0031(t-800)	

Substance	Temp. Range	Conductivity		Remarks	Ref.
		$\lambda = A_k \, e^{-E_\lambda/RT} \Omega^{-1} cm^{-1}$			
		A_k	E_λ		
$NaNO_3$	290-450	13.2	2.60 Kcal/mole		3
$NaNO_2$	320-450	13.4	3.12		
KNO_3	350-500	8.55	3.15		
$CdCl_2$	500-700	6.52	2.20		
CdI_2	400-700	25.3	6.34		

LiF

NaF

KF

Substance	Temp. Range	Conductivity		Remarks	Ref.
		$\lambda = A'_\lambda \, e^{-\Delta H^{\ddagger}/RT}$			
		A'	ΔE_λ Kcal		
Li_2CO_3	740-850	3.372	3.94_2		5
Na_2CO_3	805-970	13.757	3.87_9		
K_2CO_3	910-1010	11.014	3.89_2		
		$\Delta eq = A_B \, e^{-\Delta H^{\ddagger}/RT}$			
		A_B	E		
Li_2CO_3	740-850	755.3	4.40_0		
Na_2CO_3	865-970	493.4	4.17_6		
K_2CO_3	910-1010	544.8	4.65_1		

REFERENCES

1. Van Artsdalen and Jaffe, (1955), (1956)

2. Huber, Potter and St. Clair, (1952)

3. Bloom, Knapp, Molloy and Welch (1953)

4. Winterlagen and Warner (1956); Bockris and Crook (1957); Yim and Feinleib (1957)

5. Janz and Lorenz (1963)

Table V.

Transference Number Data

#	1	2	3	4
Salt:	$LiNO_3$	$NaNO_3$	$NaNO_3$	$NaNO_3$
$t_+(exp)$:	$0.84 \pm .06$	$0.71 \pm .01$	$0.68 \pm .05$	
$t_-(exp)$:				0.30
$t_+ = M_-/M_+ + M_-$:	0.90	0.73	0.73	0.73
$\delta t_\pm$:	-0.06	-0.02	-0.05	-0.03
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.82	0.71	0.71	0.71
$r_-(\overset{o}{A})$:	2.3	2.3	2.3	2.3
$r_+(\overset{o}{A})$:	0.60	0.95	0.95	0.95
Temp.:	350°	350°	not given	$324^o - 413^o$
Cell design:	U tube with ultra-fine disc	U tube with ultra-fine disc	KNO_3 catholyte U tube with ultra-fine disc	bubble cells & vertical capillaries
Electrodes:	Ag-AgNO$_3$ capillary connection	Ag-AgNO$_3$ capillary connection	Pt	"Na electrodes:" Ag/AgNO$_3$ external through Na conducting porcelain
Measurement:	volume change in capillary of cathode compartment	volume change in capillary of cathode compartment	analysis of catholyte for Na$^+$	volume change (bubble displacement and in capillary)
Remarks:			electrode reactions not considered	Pyrex frit, no temperature effect
Reference:	(5)	(5)	(13)	(23)

#	5	6	7	8
Salt:	NaNO$_3$	KNO$_3$	KNO$_3$	RbNO$_3$
$t_+(exp)$:		0.60$\pm$.03	0.59$\pm$.02	0.59$\pm$.04
$t_-(exp)$:	0.25$\pm$.02			
$t_+ = M_-/M_+ + M_-$:	0.73	0.61	0.61	0.42
δt_+:	+0.01	-0.01	-0.02	+0.17
$t_+ = \dfrac{r_-z_+}{r_-z_+ + z_- z_+}$:	0.71	0.63	0.63	0.61
$r_-(\overset{o}{A})$:	2.3	2.3	2.3	2.3
$r_+(\overset{o}{A})$:	0.95	1.33	1.33	1.48
Temp.:	324°-413°	350°	not given	not given
Cell design:	bubble cells & vertical capillaries	U tube with ultra-fine disc	U tube with ultra-fine disc & NaNO$_3$ catholyte	U tube with ultra-fine disc & NaNO$_3$ catholyte
Electrodes:	"Na electrodes:" Ag/AgNO$_3$ external through Na conducting porcelain	Ag/AgNO$_3$ capillary connection	Pt	Pt
Measurement:	volume change (bubble displacement and in capillary)	volume change in capillary of cathode compartment	analysis of catholyte for K$^+$	analysis of catholyte for K$^+$
Remarks:	porcelain frit, no temperature effect		electrode reactions not considered	electrode reactions not considered
Reference:	(23)	5)	(13)	(13)

#	9	10	11	12
Salt:	$CsNO_3$	$Cs\,NO_3$	$AgNO_3$	$AgNO_3$
$t_+(exp)$:	$0.59 \pm .07$	$0.398 \pm .004$		$0.72 \pm .06$
$t_-(exp)$:			$0.23 \pm .03$	
$t_+ = M_-/M_+ + M_-$:	0.32	0.32	0.36	0.36
$\delta t_\pm$:	+0.27	+.08	+0.41	+0.36
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.58	0.58	0.65	0.65
$r_-(\overset{o}{A})$:	2.3	2.3	2.3	2.3
$r_+(\overset{o}{A})$:	1.69	1.69	1.26	1.26
Temp.:	not given	460°	220°	350°
Cell design:	U tube with ultra-fine disc & $NaNO_3$ catholyte	tube with fritted disc cathode. Bulk anode compartment	Modified Hittorf cell composed of a piece of un-glazed porcelain	U tube with ultra-fine disc
Electrodes:	Pt	Ag/AgCl cathode Pt anode	Ag	Ag
Measurement:	analysis of catholyte for Cs^+	radioactive Cs^{134}	Chemical anal-yses of both compartments	volume change in capillary of cathode compartment
Remarks:	electrode reactions not considered	Ag/AgCl imbed-ded in glass wool	very poor reproducibility	
Reference:	(13)	(11)	(3)	(5)

#	13	14	15	16
Salt:	$AgNO_3$	$AgNO_3$	$AgNO_3$	$AgNO_3$
$t_+(exp)$:			$0.781 \pm .006$	$0.744 \pm .010$
$t_-(exp)$:	$0.24 \pm .05$	$0.251 \pm .014$		
$t_+ = M_-/M_+ + M_-$:	0.36	0.36	0.36	0.36
$\delta t_\pm$:	+0.40	+0.39	+0.42	+0.38
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.65	0.65	0.65	0.65
$r_-(\overset{o}{A})$:	2.3	2.3	2.3	2.3
$r_+(\overset{o}{A})$:	1.26	1.26	1.26	1.26
Temp.:	225°-275°	232°	219°	281.5^o
Cell design:	bubble cell	modified hori-zontal cell; $AgNO_3$/air con-tact Uf discs	2-compartment cell with medium disc	same as #15
Electrodes:	Ag	Ag	Ag	Ag
Measurement:	volume change	horizontal dis-placement of $AgNO_3$ in end of capillary	balance deter-mination of change in center of gravity upon passage of current	same as #15
Remarks:	no apparent temp. effect	apparently no "sticking" prob-lem	slight tempea ture effect	
References	(4)	(15)	(25)	(25)

#	17	18	19	20
Salt:	$TlNO_3$	$TlNO_3$	$NaNO_2$	KNO_2
$t_+(exp)$:	$0.60 \pm .05$	$0.306 \pm .007$	0.75 ± 0.10	0.62 ± 0.06
$t_-(exp)$:				
$t_+ = M_-/M_+ + M_-$:	0.23	0.23	0.67	0.54
δt_+:	+0.37	+0.07	+0.12	+0.08
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.61	0.61		
$r_-(\overset{o}{A})$:	2.3	2.3		
$r_+(\overset{o}{A})$:	1.44	1.44	0.95	1.33
Temp.:	not given	220°	not given	not given
Cell design:	U tube with ultra-fine disc; either Na or KNO_3 catholyte	tube with ultra-fine disc; tube with fritted disc dipping in anolyte	U tube with ultra-fine disc; KNO_2 catholyte	U tube with ultra-fine disc; $NaNO_2$ catholyte
Electrodes:	Pt	Pt	Pt	Pt
Measurement:	analysis of catholyte for Tl	determination of Tl^{204} which migrates to catholyte	analysis of catholyte for Na	analysis of catholyte for K
Remarks:	electrode reactions not considered		electrode reactions not considered	see #19
References:	[19]	[20]	[13]	[13]

#	21 LiCl	22 NaCl	23 NaCl	24 KCl
Salt:	LiCl	NaCl	NaCl	KCl
t_+(exp):			$0.87\pm.06$	
t_-(exp):	$0.25\pm.03$	$0.38\pm.04$		$0.38\pm.04$
$t_+=M_-/M_++M_-$:	0.84	0.59	0.59	0.48
$\delta t_\pm$:	-0.09	$+0.03$	$+0.28$	$+0.14$
$t_+=\dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.75	0.66	0.66	0.58
$r_-(\overset{o}{A})$:	1.81	1.81	1.81	1.81
$r_+(\overset{o}{A})$:	0.60	0.95	0.95	1.33
Temp.:	600°	860°	850°	830°
Cell design:	quartz U tube with fused quartz membrane	same as #21	modified Hittorf cell composed of vycor tube packing with salt and diatomaceous earth	quartz U tube with fused quartz membrane
Electrodes:	Pb cathode; Pb or Ag anode (same results)	same as #21	Pt anode , graphite cathode	Pb cathode; Pb or Ag anode
Measurement:	analysis of Cl^{36} migration to an-olyte	same as #21	chemical analysis of both compartments	same as #21
Remarks:			poor reproducibility	
Reference:	(9)	(9)	(7)	(9)

#	25	26	27	28	29
Salt:	KCl	RbCl	CsCl	AgCl	AgCl
t_+(exp):	$0.77 \pm .08$				
t_-(exp):		$0.42 \pm .04$	$0.36 \pm .04$	$0.15 \pm .03$	$0.19 \pm .03$
$t_+ = M_-/M_+ + M_-$:	0.48	0.29	0.21	0.25	0.25
$\delta t_\pm$:	+0.29	+0.29	+0.43	+0.60	+0.56
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.58	0.55	0.52	0.59	0.59
$r_-(\overset{o}{A})$:	1.81	1.81	1.81	1.81	1.81
$r_+(\overset{o}{A})$:	1.33	1.48	1.69	1.26	1.26
Temp.:	850°	785°	685°	650°	925°
Cell design:	same as #23	same as #24	same as #24	U cell; quartz ultra-fine pores	same as #28
Electrodes:	same as #23	same as #24	same as #24	Ag	same as #28
Measurement:	same as #23	same as #21	same as #21	migration of radioactive Cl^- to anolyte	same as #28
Remarks:	same as #23			problem of "sticki-ness" apparently not severe with Pyrex	same as #28
Reference:	(7)	(9)	(9)	(10)	(10)

#	30	31	32	33
Salt:	AgCl	TlCl	TlCl	TlCl
t_+(exp):	$0.54^{\pm}.07$			
t_-(exp):		$0.496^{\pm}.004$	$0.492^{\pm}.001$	0.493
$t_+=M_-/M_++M_-$:	0.25	0.15	0.15	0.15
$\delta t_\pm$:	+0.29	+0.34	+0.33	+0.33
$t_+=\dfrac{r_-z_+}{r_-z_++z_-z_+}$:	0.59	0.56	0.56	0.56
$r_-(\overset{o}{A})$:	1.81	1.81	1.81	1.81
$r_+(\overset{o}{A})$:	1.26	1.44	1.44	1.44
Temp.:	500°	475°	505°	525°
Cell design:	tube with fritted disc dipping in catholyte	Bubble cell	same as #31	same as #31
Electrodes:	carbon anode; Ag cathode	Tl	Tl	Tl
Measurement:	weighing of loss of weight of anolyte compartment	volume change	same as #31	same as #31
Remarks:	very poor re-producibility; "stickiness"	very slight random varia-tion with temperature	same as #31	same as #31
Reference:	(19)	(4)	(4)	(4)

#	34	35	36
Salt:	TlCl	$MgCl_2$	$CaCl_2$
t_+(exp):	$0.410+2.82\cdot$ $\cdot10^{-4}(t-430)$		
t_-(exp):		$0.52^{\pm}.04$	$0.58^{\pm}.09$
$t_+=M_-/M_++M_-$:	0.15	0.75	0.64
$\delta t_{\pm}$:	$+0.26(at430^{\circ})$	-0.27	-0.22
$t_+=\dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.56	0.85	0.79
$r_-(\overset{\circ}{A})$:	1.81	1.81	1.81
$r_+(\overset{\circ}{A})$:	1.44	0.65	0.99
Temp.:	$430-700^{\circ}$	$730-920^{\circ}$	$780-1100^{\circ}$
Cell design:	Hittorf type cell;middle compartment packed with Al_2O_3	cell with porous quartz membrane	same as #35
Electrodes:	Tl	graphite	same as #35
Measurement:	measurement of vertical displacement in capillary	Cl^{36} migration to anolyte;cell split for analysis	same as #35
Remarks:	long packing, rather loose;temp. measured inside packing;linear increase of t^+ with temperature	no temperature effect	slight linear increase of t_- with temperature
References:	(22) (21)	(12)	(12)

#	37	38	39	40
Salt:	$SrCl_2$	$BaCl_2$	$ZnCl_2$	$ZnCl_2$
t_+(exp):			$0.716-3.07\cdot$ $\cdot 10^{-4}(t-318)$	0.6 ± 0.1
t_-(exp):	$0.74 \pm .07$	$0.77 \pm .09$		
$t_+ = M_-/M_+ + M_-$:	0.45	0.34	0.52	0.52
$\delta t_{\pm}$:	-0.19	-0.11	+.20 (at 318°)	+0.10
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.76	0.73	0.83	0.83
$r_-(\overset{O}{A})$:	1.81	1.81	1.81	1.81
$r_+(\overset{O}{A})$:	1.13	1.35	0.74	0.74
Temp.:	880-1165°	960-1100°	318-700°	435-673°
Cell design:	cell with porous quartz membrane	same as #37	Hittorf type cell;middle compartment packed with Al_2O_3	Hittorf type cell with one frit
Electrodes:	graphite	same as #37	Zn	when using Zn^{65}, anode:carbon rod, cathode:W at high temp.,Hg at low temp;Cl^{36}:anode:Zn drop;cath:W-high,Hg low
Measurement:	Cl^{36} migration to anolyte;cell split for analysis	same as cell #37	measurement of vertical displacement in capillary	Zn^{65} migration from anolyte to catholyte;Cl^{36} migration from catholyte to anolyte
Remarks:	no temperature effect	same as #37	same as #34 but t^+ increases linearly with temp.	very poor reproducibility; apparently $t^-_{Cl\ run} + t^+_{Zn\ run} < 1$
References:	(12)	(12)	(21,22)	(24)

#	41	42	43	44
Salt:	$CdCl_2$	$PbCl_2$	$PbCl_2$	$PbCl_2$
$t_+(exp)$:				
$t_-(exp)$:	$0.340 \pm .007$	$0.78 \pm .03$	0.83	$0.758 \pm .014$
$t_+ = M_-/M_+ + M_-$:	0.39	0.26	0.26	0.26
$\delta t_\pm$:	$+0.27$	-0.04	-0.09	$-.02$
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.72	0.73	0.73	0.73
$r_-(\text{Å})$:	1.81	1.81	1.81	1.81
$r_+(\text{Å})$:	1.43	1.32	1.32	1.32
Temp.:	$602-608^\circ$	$520-680^\circ$	$550-580^\circ$	565°
Cell design:	horizontal cell	cell with asbestos disc	cell with corundum dust diaphragm	bubble cell, ultra-fine disc or packed asbestos
Electrodes:	Cd		Pb	Pb
Measurement:	displacement of electrolyte;Cd interface in horizontal capillary	analysis of the two compartments	same as #42	volume change bubble displacement
Remarks:	Murgulescu and Marta (18) could not determine transport no. of Cd^{++} in a bubble cell due to dissolution of Cd in $CdCl_2$	poor reproducibility		
References:	(14)	(16)	(17)	(1)

#	45	46	47
Salt:	$PbCl_2$	$PbCl_2$	$PbCl_2$
$t_+(exp)$:			
$t_-(exp)$:	$0.757\pm.002$	$0.393\pm.01$	$0.382\pm.01$
$t_+ = M_-/M_++M_-$:	0.26	0.26	0.26
$\Delta t_\pm$:	-.02	+0.35	+0.36
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.73	0.73	0.73
$r_-(\overset{o}{A})$:	1.81	1.81	1.81
$r_+(\overset{o}{A})$:	1.32	1.32	1.32
Temp.:	635°	$527-529^o$	$602-608^o$
Cell design:	same as #44	horizontal cell	same as #46
Electrodes:	Pb	Pb	Pb
Measurement:	same as #44	displacement of electrolyte;Pb interface in horizontal capillary	same as #46
Remarks:	t_-: coarse disc = 0.366; medium=0.669;fine =0.711 no apparent temp. effect, some leakage	Pb in contact with air:stickiness (see Ref. 18)	same as #46
Reference:	(2)	(14)	(14)

#	48	49	50
Salt:	$PbCl_2$	$PbCl_2$	$PbBr_2$
t_+(exp):	0.24±.04		
t_-(exp):		0.73±.03	0.92
$t_+ = M_-/M_+ + M_-$:	0.26	0.26	0.44
$\delta t_\pm$:	-.02	+0.01	-0.36
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.73	0.73	0.75
$r_-(\overset{o}{A})$:	1.81	1.81	1.95
$r_+(\overset{o}{A})$:	1.32	1.32	1.32
Temp.:	550°	not given	430°
Cell design:	moving boundary cell, U tube with frit and capillary	bubble cell	same as #43
Electrodes:	carbon	Pb	Pb
Measurement:	measurement of displacement in anolyte towards catholyte of $PbCl_2$-$ZnCl_2$ interface; $ZnCl_2$ follows $PbCl_2$	volume change; bubble displacement	same as #42
Remarks:		poor reproducibility	no indication of reproducibility
Reference:	(6)	(19)	(17)

#	51	52
Salt	$PbBr_2$	$PbBr_2$
t_+(exp):		
t_-(exp):	$0.653 \pm .013$	$0.674 \pm .003$
$t_+ = M_-/M_+ + M_-$:	0.44	0.44
$\delta t_\pm$:	-0.10	-0.12
$t_+ = \dfrac{r_- z_+}{r_- z_+ + z_- z_+}$:	0.75	0.75
$r_-(\AA)$:	1.95	1.95
$r_+(\AA)$:	1.32	1.32
Temp.:	500°	600°
Cell design:	bubble cell	same as #51
Electrodes:	Pb	Pb
Measurement:	volume change; bubble displacement	same as #51
Remarks:		
Reference:	(4)	(4)

REFERENCES

1. Duke and Laity (1954)

2. Duke and Laity (1955)

3. Duke and Cook (1957)

4. Laity and Duke (1958)

6. Duke and Cook (1958)

7. Duke and Cook (1958)

8. Duke and Fleming (1959)

9. Duke and Bowman (1959)

10. Duke, Bowman, Wolf and Garfinkel (1960)

11. Murgulescu and Topor, in press

12. Wolf (1961)

13. Duke and Victor (in press, 1962)

14. Bloom and Doull (1956)

15. Bloom and James (1959)

16. Karpachev and Pal'guev (1949)

17. Delimarskii, Turov and Gitman (1955)

18. Lorenz and Janz (1957)

19. Murgulescu and Marta (1960)

20. Murgulescu and Topor (1962)

21. Klemm (1961)

22. Fisher and Klemm (1961)

23. Labrie and Lamb (1961)

24. Lunden (1962)

Table VI Tracer Diffusion in Molten Salts and Oxides

#	Melt	Ion	D × 10⁵	D_o	E	Temp. or Temp. Range	Method	Remarks	Ref.
1	$LiNO_3$	Li^+	2.93(350°)	$2.47 \cdot 10^{-3}$	5490±110	264-320	marked material in fused silica capillary;Li^6,N^{15},O^{18}	D% error: Li=1.5, NO_3=2.5;Nernst Einstein eq. not obeyed;Λ calculated 30% too high;r_{++} very small	9
2		NO_3^-	1.15(350°)	$1.95 \cdot 10^{-3}$	6340±270				
3	$NaNO_3$	Na^+	2.33(350°)	$1.29 \cdot 10^{-3}$	4970±80	313-376	marked material in fused silica capillary;Na^{22},N^{15},O^{18}	D% error:Na=1.5, NO_3=1.0;Nernst-Einstein eq. not obeyed	9
4		NO_3^-	1.48(350°)	$0.90 \cdot 10^{-3}$	5080±80				2
5	KNO_3	K^+	1.52(350°)	$1.32 \cdot 10^{-3}$	5530±200	344-389	marked material in fused silica capillary;K^{41},N^{15},O^{18}	D% error: K=1.5, NO_3=1.5;Nernst-Einstein eq. not obeyed	9
6		NO_3^-	1.35(350°)	$1.42 \cdot 10^{-3}$	5760±260				
7	$CsNO_3$	Cs^+	1.22(350°)	$1.13 \cdot 10^{-3}$	5610±270	428-478	marked material in fused silica capillary;Cs^{134},N^{15},O^{18}	D% error: Cs=1.5, NO_3=1.5;Nernst-Einstein eq. not obeyed	9
8		NO_3^-	1.11(350°)	$1.78 \cdot 10^{-3}$	6280±380				
9	$AgNO_3$	Ag^+	2.40(350°)	$0.49 \cdot 10^{-3}$	3730±80	219-289	marked material in fused silica capillary;Ag^{110},N^{15},O^{18}	D% error: Ag=4.0, NO_3=1.0;Nernst-Einstein eq. not obeyed**	9
10		NO_3^-	1.40(350°)	$0.31 \cdot 10^{-3}$	3840±370				9
11	Na_2CO_3	Na^+	19.2±0.4			895	tracer diffusion (Na^{22} & C^{14}) from a suspended diaphragm into a stirred inactive bulk	calibrated with $NaNO_3$; labyrinth factor taken into account;Nernst-Einstein eq. not applicable;calculated r_{--} negative;large $D_{CO_3^=}$ could be due to $CO_3^= \rightleftharpoons CO_2 + O^=$ equilibrium	10
12		$CO_3^=$	27.9±0.9						
13	$NaCl$	Na^+		$8 \cdot 10^{-4}$	4000	845-916	Na^{22} & Cl^{36} diffusion out of capillary into inactive melt	absolute error in D=7%;D_o=$23 \cdot 10^{-4}$ exp(-7166/RT) if not corrected for length; direct calculation of Λ by Nernst-Einstein eq. gives results 40% too high	3
14		Cl^-		$33 \cdot 10^{-4}$	8500	825-942			

** Λ calculated 65% too high

#	Melt	Ion	D × 10^5	D_o	E	Temp. or Temp. range	Method	Remarks	Ref
15 16	NaCl	Na$^+$ Cl$^-$		3.36·10^{-3} 3.02·10^{-3}	7860±110 8390±40	830-990	Na^{22} & Cl^{36} diffusing from a tagged reservoir into a non-active capillary	D$_{Cl}$ agrees with above; D$_{Na}$ much lower with a much higher activation energy; discrepancy accounted for by authors to short diffusion times used by Ref.(3)	11
17 18	RbCl	Rb$^+$ Cl$^-$		2.51·10^{-3} 1.67·10^{-3}	8010±30 7420±70	740-880	Rb^{86} & Cl^{36} diffusing from a tagged reservoir into a non-active capillary	Transport no. calculated from derived diffusion coefficient (Nernst-Einstein eq.) discrepancy taken into account)(calculated also for NaCl)	11
19 20	CsCl	Cs$^+$ Cl$^-$		1.73·10^{-3} 2.46·10^{-3}	7320±50 7820±80	668-794	Cs^{134} & Cl^{36} diffusing from a tagged reservoir into a non-active capillary	Transport no.-transport no. calculated from derived diffusion coefficient (Nernst-Einstein eq.) discrepancy taken into account)(calculated also for NaCl)	11
21 22	NaI	Na$^+$ I$^-$		0.63·10^{-3} 0.43·10^{-3}	4030±50 4420±60	670-806	Na^{22} & I^{131} diffusing from a tagged reservoir into a non-active capillary	transport no. calculated from derived diffusion coefficient (Nernst-Einstein eq. discrepancy taken into account)(calculated also for NaCl);temp. coefficient of r$_{++}$=0	11
23	TlCl	Tl$^+$	5.04·10^{-5}(577°)	7.6·10^{-4}	4600	487-577	Tl^{204} diffusion out of capillary into inactive melt	20-70 hour runs; accuracy not indicated	1

#	Melt	Ion	D × 10⁵	D_o	E	Temp. or Temp. range	Method	Remarks	Ref.
24	$PbCl_2$	Pb^{++}	$1.06 \cdot 10^{-5}(530°)$ $1.07 \cdot 10^{-5}(540°)$ $1.49 \cdot 10^{-5}(530°)$ $2.06 \cdot 10^{-5}(540°)$	$9.28 \cdot 10^{-5}$	3503 ± 155	510-570	Pb^{210} & Cl^{36} diffuse out of capillary into inactive melt	D_{Cl} has a break around 540°; polymerization suggested; Λ calc. from Nernst-Einstein eq. too high	8
25		Cl^-		$3.68 \cdot 10^{-5}$	8576 ± 325	510-570			8
26	$PbCl_2$	Pb^{++}	$1.0 \pm .02 \cdot 10^{-5}$ $(510°)$	$7.73 \cdot 10^{-4}$	6777 ± 643		Pb^{210} & Cl^{36} diffuse out of capillary into inactive melt	the break observed in Ref. 8 for D_{Cl} does not appear in this re-determination	6
27		Cl^-	$1.80 \pm .05 \cdot 10^{-5}$ $(510°)$	$8.95 \cdot 10^{-4}$	6099 ± 483	510-566			6
28	$PbCl_2 \cdot KCl$ 1)25.2 mole % KCl	Pb^{++}	$0.99 \pm .04 \cdot 10^{-5}$ $(530°)$	$5.03 \cdot 10^{-3}$	9864 ± 242	448-575	Pb^{210} & Cl^{36} diffuse out of capillary into inactive melt	E varies with composition of the melt for D_{Pb} but not for D_{Cl}	7
29		Cl^-	$2.42 \pm .11 \cdot 10^{-5}$ $(530°)$	$2.34 \cdot 10^{-3}$	7406 ± 541				7
30	$PbCl_2 \cdot KCl$ 2)33.3 mole % KCl	Pb^{++}	$.82 \pm .08 \cdot 10^{-5}$ $(524°)$	$2.92 \cdot 10^{-3}$	12796 ± 1092	448-575	Pb^{210} & Cl^{36} diffuse out of Pyrex capillary into inactive melt	fluctuations of D_{Pb} & D_{Cl} at this composition ($2PbCl_2 \cdot KCl$)	7
31		Cl^-	$1.95 \pm .29 \cdot 10^{-5}$ $(524°)$	$1.44 \cdot 10^{-3}$	6608 ± 572				
32	$PbCl_2 \cdot KCl$ 3)37.0 mole % KCl	Pb^{++}	$.94 \pm .04 \cdot 10^{-5}$ $(520°)$	$1.96 \cdot 10^{-3}$	8405 ± 566	448-575	Pb^{210} & Cl^{36} diffuse out of Pyrex capillary into inactive melt	See # 28, 29	7
33		Cl^-	$2.56 \pm .04 \cdot 10^{-5}$ $(520°)$	$1.31 \cdot 10^{-3}$	6443 ± 417				7
34	$CdCl_2 \cdot KCl$	Cd^{++}	$1.40 \cdot 10^{-5}$			469-471	interdiffusion of two columns of molten salt in capillary; Cd^{115} tracer		4
35	$CdCl_2$	Cd^{++}	$2.60 \cdot 10^{-5}$			585-595	Cd^{115} & Cl^{36} diffusing out of capillary	experiment done also with Cd dissolved in melt; relatively little effect on D	12
36		Cl^-	$2.40 \cdot 10^{-5}$						12
37	$ZnBr_2$	Zn^{++}	$3.46 \cdot 10^{-6}$ $(at\ 400°)$	$79 \cdot 10^{-3}$	16,060	400-640	Zn^{65} diffusion out from an open end capillary	very long diffusion times	5

#	Melt	Ion	$D \times 10^5$	D_o	E	Temp. or Temp. range	Method	Remarks	Ref.
38	$ZnBr_2$	Zn^{++}	$0.26 \cdot 10^{-6}$ (at 400°)	$4.05 \cdot 10^{-1}$	19,000	400-565	diffusion into each other in a capillary of two columns (one with radioactive material)	data could be adapted to a parabolic curve giving; E=20,600 at 450° and 14,300 at 550°	13
39	slag by wt:39% CaO,40% SiO_2,21% Al_2O_3	Ca^{++}	$3.5 \cdot 10^{-7}$ $2.1 \cdot 10^{-6}$ $3.4 \cdot 10^{-6}$		~70 Kcal	1350 1500 1540	Ca^{45} diffusion out from an open capillary	Both methods for Si81 gave the same result; high diffusion of Si81 precludes a simple ionic movement (with Si^{++} or Si^{+4}) since then $t_{Si} \simeq .10$;mechanism with no transfer of charge; investigation with O18 would be interesting	16
40		Si	$4.7 \cdot 10^{-8}$ $1.05 \cdot 10^{-7}$		~70 Kcal	1365 1430	Si^{81} diffusion out from an open capillary and also from reservoir into capillary		
41	$FeO \cdot SiO_2$ 61% by wt. FeO	Fe^{++}	$7.9 \pm 3 \cdot 10^{-5}$ $9.6 \pm 2 \cdot 10^{-5}$ $12.0 \pm 1.0 \cdot 10^{-5}$		40 Kcal	1250 1275 1304	Fe^{59} from radioactive reservoir into inactive capillary	activation energy for conduction;16 Kcal mobility μ at 1250° using Nernst-Einstein relationship;$D_{Fe} = 5.8 \pm 1.3 \cdot 10^{-5}{}_{Fe}$ see (14)	15
42	$Na_2O \cdot 2SiO_2$ (66.6 mole % SiO_2)	Na^+	$3.24 \cdot 10^{-5}$ (1200°)		11.93 Kcal	970-1210	Na^{24} diffusion from a point source through the capillary	both alundum and graphite capillaries of various diameters were used (different wetting properties);no dependence on the diameter of the capillary found (3-8 mm);no difference found between alundum and graphite	20

REFERENCES

1. Berne and Klemm (1953)

2. Van Artsdalen, Brown, Dworkin and Miller (1956)

3. Borucka, Bockris and Kitchener (1957)

4. Angell and Bockris (1958)

5. Wallin and Lunden (1959)

6. Perkins, Escue, Lamb, Tidwell and Wimberley (1960)

7. Perkins, Escue, Lamb, Tidwell and Wimberley (1960)

8. Perkins, Escue, Lamb, Tidwell and Wimberley (1960)

9. Dworkin, Escue and Van Artsdalen (1960)

10. Djordjevic and Hills (1960)

11. Bockris and Hooper (1961)

12. Angell and Tomlinson (1961)

13. Wallin (1962)

14. Simnad, Yang and Derge (1956)

15. Yang, Chien and Derge, unpublished report

16. Towers and Chipman (1957)

17. Wallin (1962)

18. Berne and Berggren (1960)

19. Carman and Stein (1956)

20. Malkin and Mogutnov (1960)

21. Topol and Osteryoung (1962)

Table VII Interdiffusion Coefficients in Molten Salts

#	Ion	Melt	Concentration	$D \times 10^5$	Temp.	E Kcal	Temp. Range.	Method	Remarks	Ref
1	Ag^+	KNO_3	not given	4.8	390			not given	quoted by Delimarskii (11)	1
2	Ag^+	$NaNO_3$	$1.9 \cdot 10^{-2}$ m mole/g	$3.25 \pm .02$	400	$4.5 \pm .1$	313-430	chronopoten.; Sand eq. $\mathcal{J}$=0.15-3 sec;0.1-100 μa	quite reproducible;problem with trace impurities	10
3	Ag^+	$CsNO_3$	$1.5 \cdot 10^{-2}$ m mole/g	2.48	400	$5.1 \pm .1$	411-644			
4	Ag^+	$NaNO_3$-KNO_3 eutectic	$2 \cdot 10^{-2}$ moles/1	1.59	316	6.3	274-316	chronopoten.; $\mathcal{J}$ = 1 sec	dependence of E on temp.;D=0.4.·10-5 at 250° obtained from cathode overpotential	9
			$8 \cdot 10^{-3}$ moles/1	1.09	274					
			$10 \cdot 10^{-3}$ moles/1	0.72	263	21.7	250-263			
				0.40	250					
5	Ag^+	$NaNO_3$-KNO_3	not given	4.0	300			based on the determination of the variation of current with time for a linear diffusion toward plane electrode	$i_t = nFcA\sqrt{\dfrac{D}{\pi t}}$ used; Ecal=8.1 Kcal (3000-4000)	3
				11.0	400					
6	Tl^+	KNO_3	not given	3.4	380			not given	quoted by Delimarskii (11); see #1	1
7	Pb^{++}	$NaNO_3$-KNO_3 eutectic	$5 \cdot 10^{-3}$ moles/1	0.23	264			chronopoten.; $\mathcal{J}$ = 1 sec	melt well dried	9
8	Pb^{++}	$LiNO_3$-$NaNO_3$ KNO_3 eutectic	$1-18 \cdot 10^{-2}$ moles/1	$0.18 \pm .01$	160	13.0	160-220	polarograph. D.M.E.	Pb^{++} (hydrated) D lower, E higher than in aqueous solutions	2
9	Cd^{++}	$NaNO_3$-KNO_3 eutectic	$5 \cdot 10^{-3}$ moles/1	0.51	264			chronopoten.; $\mathcal{J}$ = 1 sec	melt dry	9
	Cd^{++}	$LiNO_3$-$NaNO_3$ KNO_3 eutectic	$1-17 \cdot 10^{-2}$ moles/1	$0.15 \pm .02$	160	13.0	160-220	polarograph. D.M.E.	Cd^{++} (hydrated) see also #8	2

#	Ion	Melt	Concentration	D × 10⁵	Temp.	E Kcal	Temp. Range	Method	Remarks	Ref
10	Ni⁺⁺	LiNO₃-NaNO₃ KNO₃ eutectic	1-17·10⁻² moles/l	0.12±.02	160	10.0	160-220	polarograph. D.M.E.	see #8	2
11	Zn⁺⁺	LiNO₃-NaNO₃ KNO₃ eutectic	1-18·10⁻² moles/l	0.15±.02	160	9.5	160-220	polarograph. D.M.E.	see #8	2
12	Ag⁺	KBr	not given	4.9	780			not given	see #1	1
13	Ag⁺	KI	not given	5.0	780			not given	see #1	1
14	Tl⁺	KBr	not given	4.2	770			not given	see #1	1
15	Tl⁺	KI	not given	3.3	780			not given	see #1	1
16	Ag⁺	LiCl-KCl	not given	4.6 / 6.6	480 / 740			not given / not given	see #1; $E = 2.2$Kcal(480°-740°)	1
17	Ag⁺	LiCl-KCl	1.4-1.7 m mole/g	2.4±.3	400	5.8±.2	374-746	chronopoten. $\mathcal{J}=.15$-3 sec 0.1-100 μa	variation in D high due to difficulty in determining conc; results of Ref.(1) not quoted	10
18	Ag⁺	LiCl-KCl eutectic	2-70 millimolar	2.6	450			chronopoten. $\mathcal{J}<5$ sec;graphic recorder	no change in D with decreasing conc.,as observed by Dalimarskii (11)	7
19	Tl⁺	LiCl-KCl	not given	3.5	580			not given	see #1	1
20	Tl⁺	LiCl-KCl	10-70 millimolar	3.88	450			chronopoten. same as Ref.(7)	no conc. effect on D	8
21	Cu⁺	LiCl-KCl eutectic	5-20 millimolar	6.68	450			limiting current; diffusion layer evaluated from $PbCl_2$ & AgCl	$i_L = \dfrac{nFDN_s}{l}$ diffusion layer $=1.8\cdot10^{-3}$cm	5

#	Ion	Melt	Concentration	D x 10^5	Temp.	E Kcal	Temp. Range	Method	Remarks	Ref
22	Cu^+	LiCl-KCl eutectic	2-70 millimolar	3.5	450			chronopoten. same as #18	comparison with #21 not made	7
23	Fe^{++}	CaCl$_2$-NaCl	0.02-9.4 mole %	2.36	600			chronopoten.		6
24	Co^{++}	LiCl-KCl eutectic	10-70 millimoles/l	2.42	450			chronopoten. same as Ref.(7)	no conc. effect on D	8
25	Ni^{++}	LiCl-KCl eutectic	2.5-10 millimolar	4.14	450			limiting current see #21	indirect method using PbCl$_2$ and AgCl values	5
26	Cd^{++}	LiCl-KCl eutectic	2.5-20 millimolar	2.75	450			limiting current see #21		5
27	Cd^{++}	LiCl-KCl eutectic	2-70 millimoles/l	1.7	450			chronopoten. $\mathcal{J}$<5 sec;graphic recorder	may be some convection problem	7
28	Cd^{++}	LiCl-KCl eutectic	10-70 millimoles/l	2.08	450			chronopoten. same as Ref.(7)		8
29	Cd^{++}	LiCl-KCl eutectic	5.9 millimoles/l	1.2±.2	400	6.5±.3	395-809	chronopoten. 0.1-100μa		10
30	Pb^{++}	LiCl-KCl	not given	4.4	720			not given	quoted by Delimarskii (11)	1
31	Pb^{++}	LiCl-KCl eutectic	10-70 millimoles/l	2.18	450			chronopoten. same as Ref.(7)		8
32	Pb^{++}	LiCl-KCl eutectic	1.26 millimoles/l	.89±.2	400	7.9±.1	381-735	chronopoten. 0.1-100μa	calculated using E=7.9, D$_{450}$=1.35·10^{-5}, D$_{720}$=5.6·10^{-5}	10
33	Bi^{+3}	LiCl-KCl eutectic	10-70 millimoles/l	0.6	450			chronopoten. $\mathcal{J}$<5 sec;graphic recorder		7

#	Ion	Melt	Concentration	$D \times 10^5$	Temp.	E Kcal	Temp. Range	Method	Remarks	Ref
34	Bi^{+3}	LiCl-KCl eutectic	0.2-1.9 millimolar	0.63±.1	400	9.8±1.0	364-657	chronopoten. 0.1μa		10
35	Bi^+	Bi-BiBr$_3$	*saturated* 0.2 & 2.1 mole %Bi	0.30·10⁻⁵ (240°)			240-285	chronopoten.	W indicating electrode;Bi-Br₃ reference electrode	12
36	U^{+4}	LiCl-KCl eutectic	5.3 millimoles/1	0.49	400	7.7	420-621	chronopoten. 0.1μa		10

REFERENCES

1. Lorenz (1922)

2. Steinberg and Nachtrieb (1950)

3. Delimarskii, Markov and Berenblium (1953)

4. Delimarskii (1954)

5. Drossbach and Petrick (1954)

6. Wood (1957)

7. Laitinen and Ferguson (1957)

8. Laitinen and Gaur (1958)

9. Inman and Bockris (1962)

10. Thalmayer, Bruckenstein and Gruen (in press)

11. Delimarskii and Markov (1961)

12. Topol and Osteryoung (1962)

TableVIII. Thermoelectric Properties

Salt	$^{\circ}K$	S_m	$-\sqrt{\widetilde{F}}\, d\widetilde{\eta}/dT$	$\bar{\bar{S}}_m{}^{\nu^+}$	Ref.
$AgNO_3$	500	13.37	7.6	21.0	1,2,3
$AgCl$	800	16.43	9.3	26	3,4
$AgBr$	750	16.00	4	27	3,4
AgI	850	16.84	10	27	3,4
$ZnCl_2$	600	14.41	-6	8	5
$SnCl$	600	20.59	+1	22	5
$CaCl$	800	14.00	-10	24.2	6

References

1. Sundheim and Rosenstreich (1959)

2. H. Holtan (1953) ; (1952)

3. Schneebaum (1962)

4. Markov (1956)

5. Poincaré (1890)

6. Nichols and Langford

Table IX. Test of Corresponding States Theorem

Salt	r_1/r_2	m_1/m_2	$r_1 - r_2$	$(r_1 + r_2) \cdot T_M$
KCl	0.733	1.12	3.14	3.3
RbBr	0.76	1.06	3.43	3.27
CsCl	0.78	1.04	3.85	3.44

Figure 1
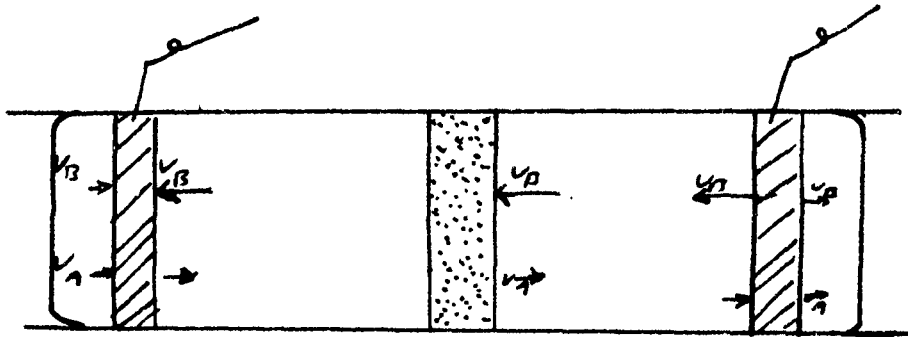
Schematic diagram of Hittorf transference number cell.

The cell contains a pair of electrodes with provisions (not shown) for correcting for volume changes and a porous diaphragm which represents the lumped frictional resistance of the entire cell. The positive and negative ions stream in opposite directions between the electrodes. An overall lateral shift is ordinarily observed experimentally.

Figure 2
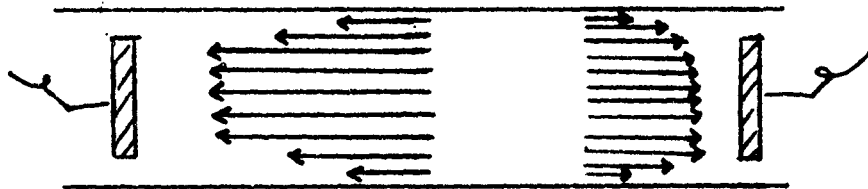
Velocity profile of ions during electrolysis. Each species has zero velocity at the wall and its own characteristic velocity in the bulk. Each species therefore is in a state of shear through a boundary layer, but the states of shear may be different.

Figure 3
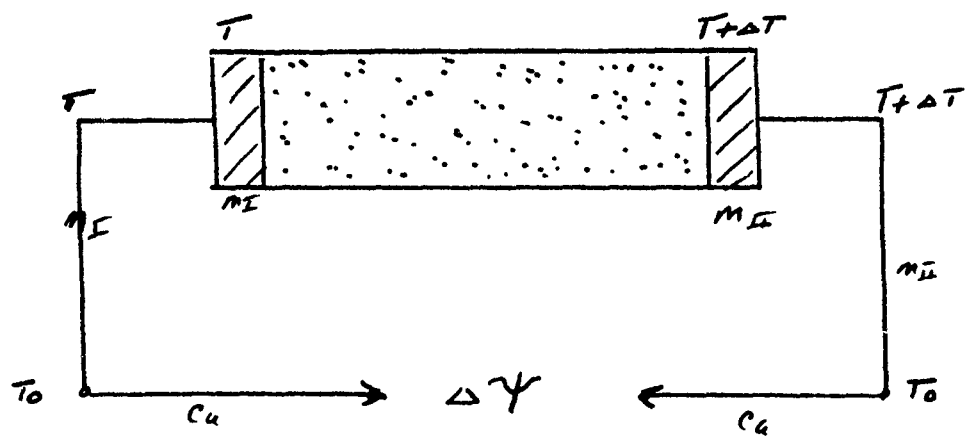
Schematic diagram of cell for determining the thermoelectric potential.

Figure 4
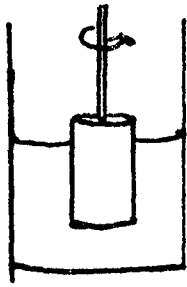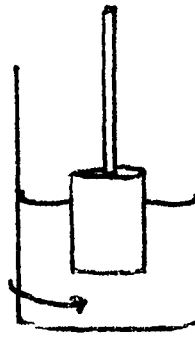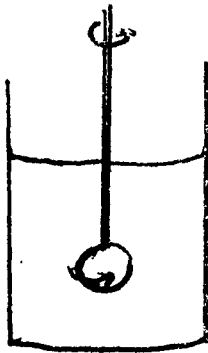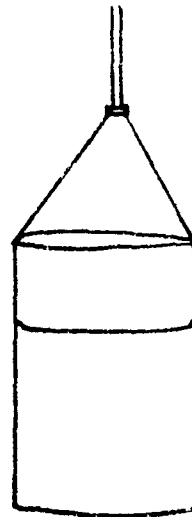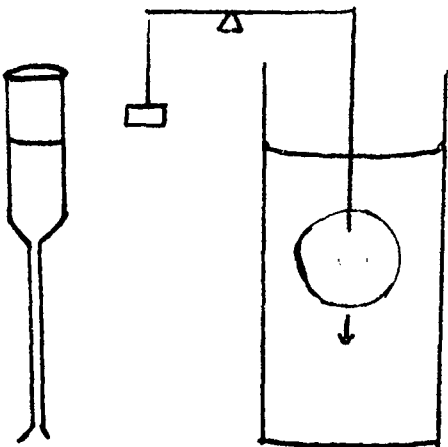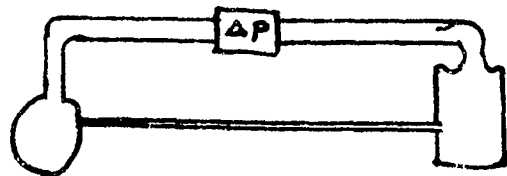
Legend to Figure 4

Schematic diagrams of methods of determining viscosity

a. Measure velocity of cylinder for fixed torque
        Rait and Hay (1938)

b. Measure torque on cylinder for fixed velocity of crucible
        Bockris and Lowe (1953)

c. Measure damping of oscillating bob
        Lorenz and Hochberg (1916)

d. Measure damping of oscillating crucible
        Barfield and Kitchener (1954)

e. Measure velocity through capillary under gravity
        Bloom, Harrap and Heymann (1948)

f. Measure velocity of partially counterbalanced falling body

    Mackenzie (1956)

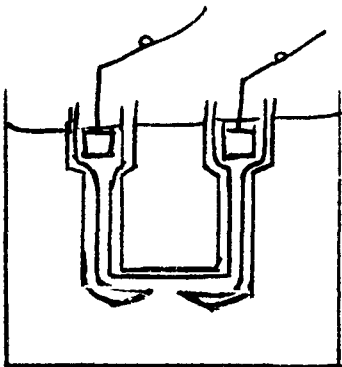g. Measure flow through capillary under applied pressure
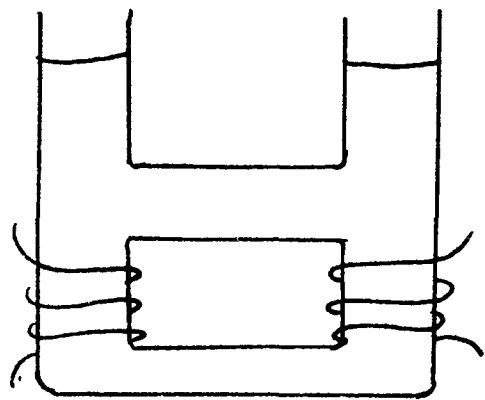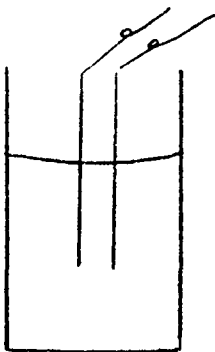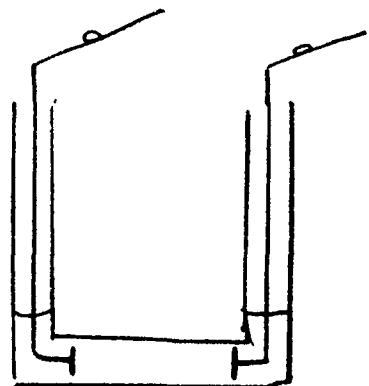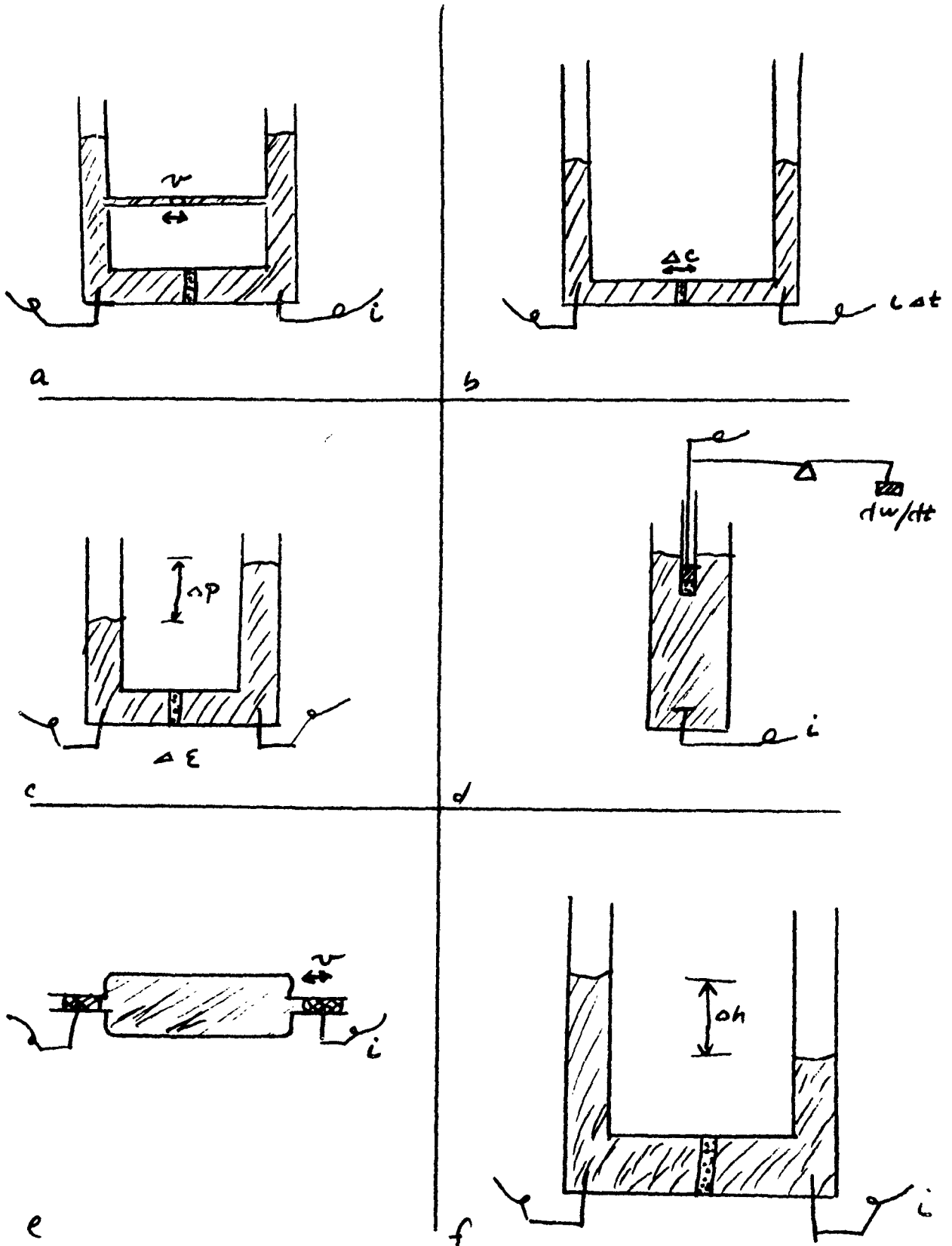   Spells (1936)

Figure 5
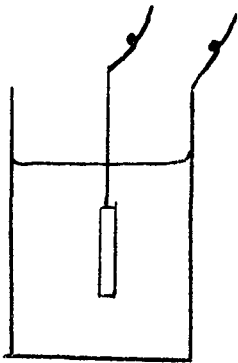
a
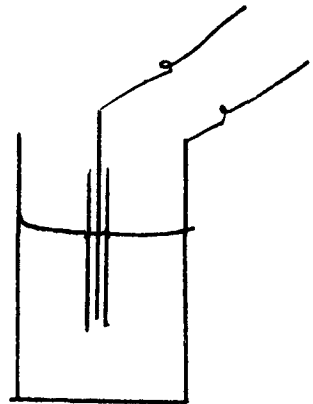
b

c

d

e
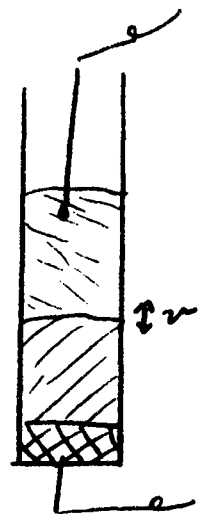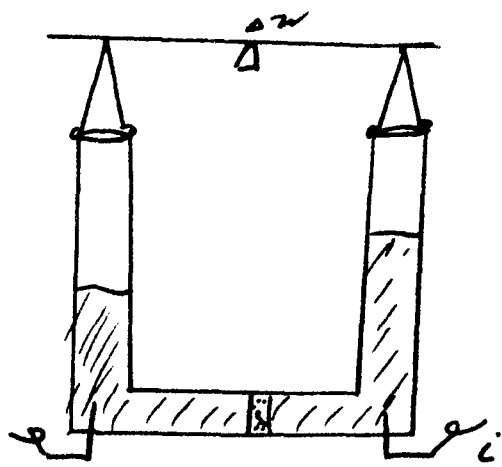
f

References for Figure 5

a. Bockris, Kitchener, Ignatiewicz and Tomlinson (1952)

b. Poincaré (1890)

c. Van Artsdalen and Jaffe (1955)

d. Yosim (1962)

e. Bronstein, Dworkin and Bredig (1962)

f. Janz and McIntyre (1960)

Figure 6

g

h

Legend to Figure 6

Schematic diagrams of methods of determining transference numbers

a. Measure velocity of bubble
        Duke and Laity (1954)

b. Measure transfer of tracer
        Duke and Cook (1958)

c. Measure piezelectric coefficient
        Kellogg and Duby (1962)

d. Measure change in weight
        Harrington and Sundheim (1957)

e. Measure translation of liquid metal electrodes
        Bloom and Doull (1956)

f. Measure steady state level
        Klemm (1961)

g. Measure change in weight
        Kellogg and Duby (1962)

h. Measure moving boundary
        Duke and Cook (1958)

Figure 7
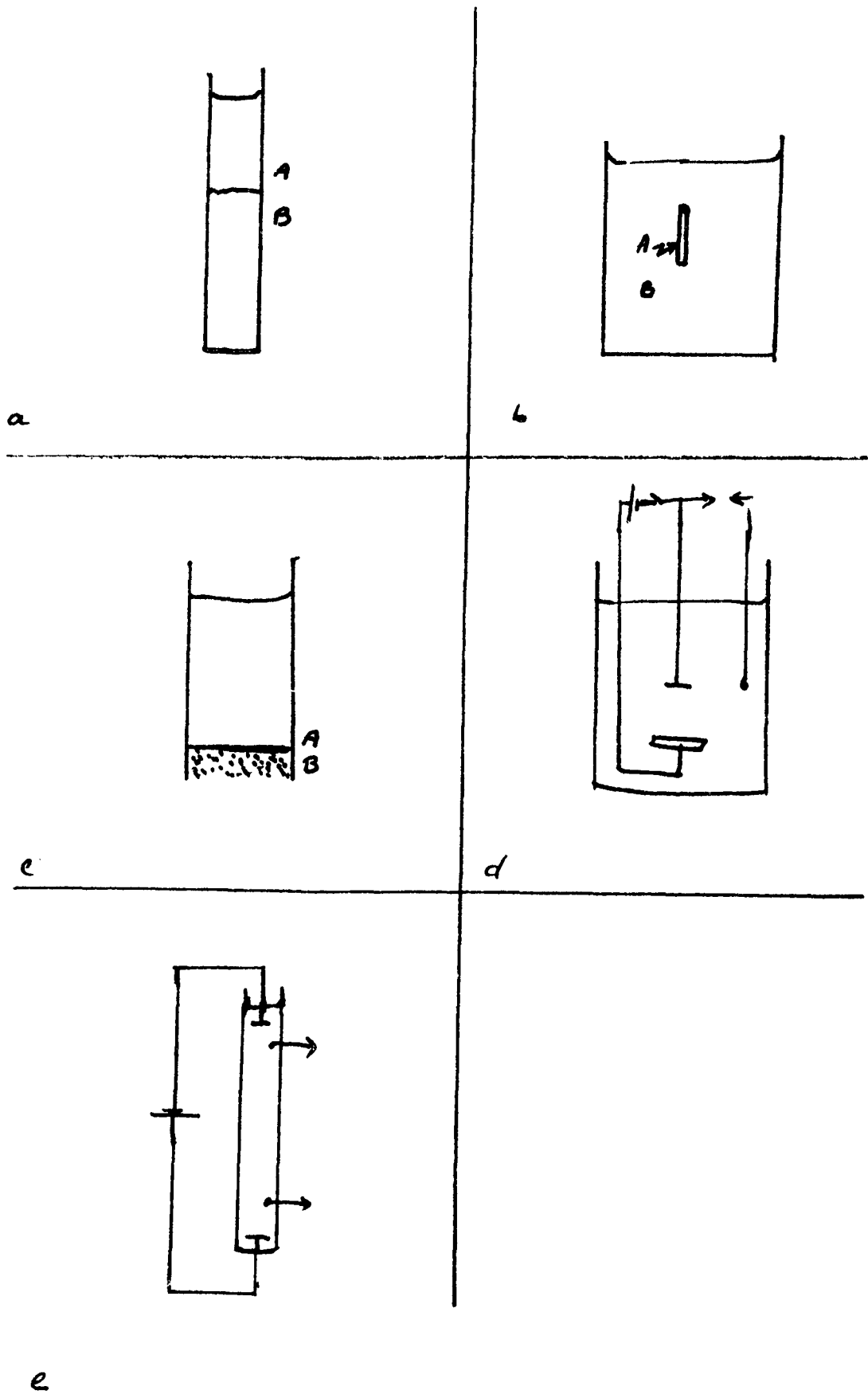
Legend to Figure 7

Schematic diagrams of methods of measuring diffusion coefficients

a. Diffusion couple--measure final composition
        Angell and Bockris (1958)

b. Open capillary--measure rate of appearance of A in B
        Angell and Tomlinson (1961)

c. Diaphragm diffusion--measure rate of appearance of B in A
        Djordjevic and Hills (1960)

d. Chronopotentiometry--measure voltage vs. time when current pulse
    is gms/vol.

e. Electromigration--measure emf at steady state

Figure 8
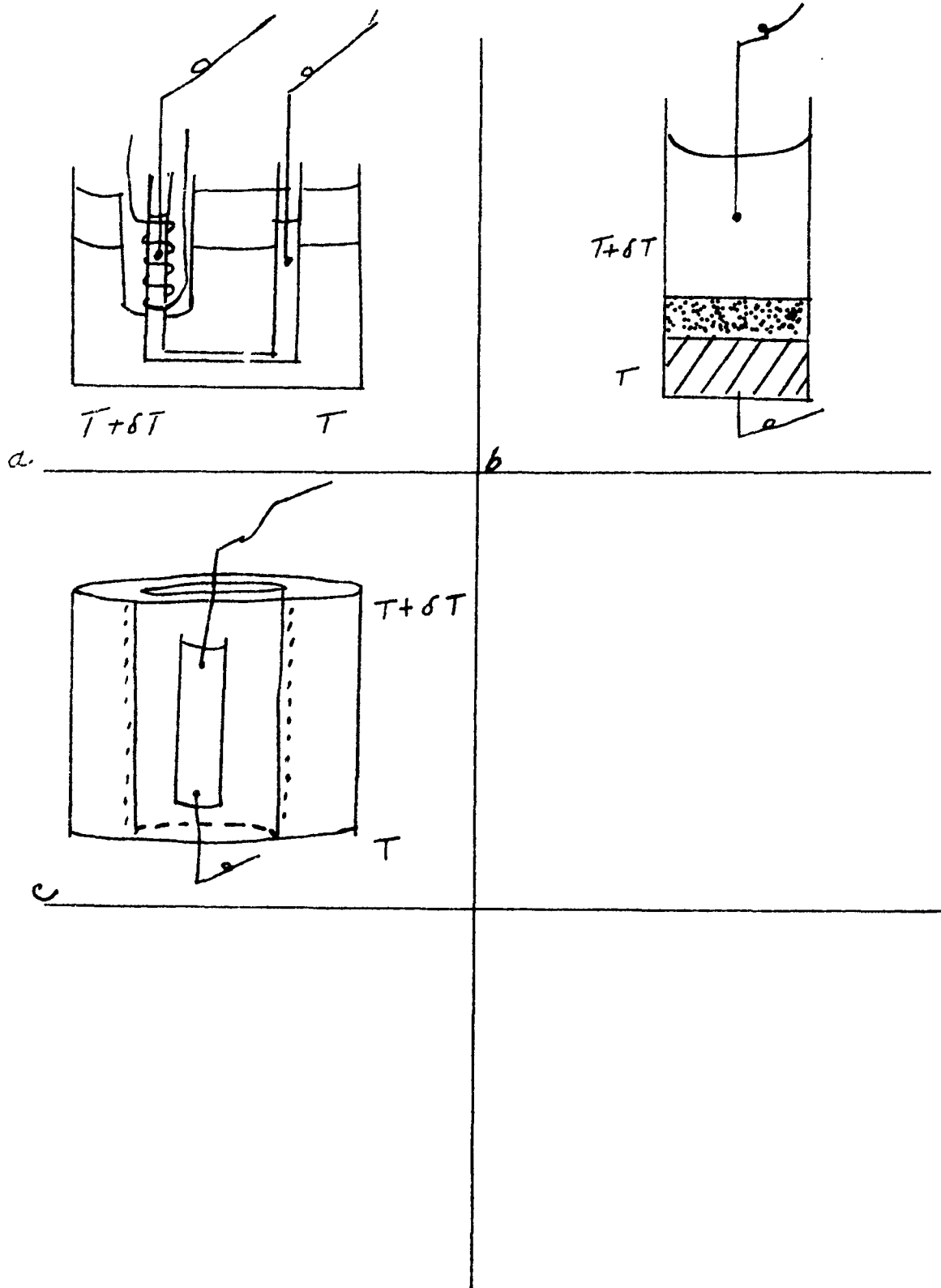
Legend to Figure 8

Schematic diagrams of methods of determining thermoelectric properties

a. Measure $\Delta\psi/\Delta T$

        Schneebaum and Sundheim (1960)

b. Measure $\Delta\psi/\Delta T$

        Milner and Sundheim (1963)

c. Measure $\int (d\psi/dT)\ dX$ and/or $\int (d\ln c/dT)\ dX$

        Sauerwein and Sundheim (1963)

BIBLIOGRAPHY

Agar in Structure of Electrolytic Solutions, W.J. Hamer, ed., Wiley, (1959)

J.S. Anderson and K. Saddington, J. Chem. Soc. 5381 (1949)

C.A. Angell and J.O'M. Bockris, J. Sci. Instruments 35, 458 (1958)

C.A. Angell and J. W. Tomlinson, Disc. Far. Soc. 32, 237 (1961)

S. Bajesy, M. Malinovsky and K. Matasovsky, Electrochim. Acta 7, 543 (1962)

Barfield and Kitchener, J. Metals, N.Y. 6, 1060 (1954)

R.J. Bearman, J. Phys. Chem. 65, 1961 (1961)

E. Berne and Berggren, Acta Chim. Scand. 14, 428 (1960)

E. Berne and A. Klemm, Zeit fur Naturforsch 8a, 400 (1953)

H. Bloom and N.J. Doull, J. Phys. Chem. 60, 620 (1956)

H. Bloom, B.J. Harrap and E. Heymann, Proc. Roy. Soc. A194, 237 (1948)

H. Bloom and D.W. James, J. Phys. Chem. 63, 757 (1959)

H. Bloom, Knapp, Molloy and Welch, Trans. Far. Soc. 49, 1458 (1953)

J. O'M. Bockris, E.H. Crook, H. Bloom and N.E. Richards, Proc. Roy.
          Soc. A255, 558 (1960)

J. O'M. Bockris and J.W. Hooper, Disc. Far. Soc. 32, 218 (1961)

J. O'M. Bockris, Kitchener, Ignatiewicz and Tomlinson, Trans. Far. Soc.
          48, 75 (1952)

J. O'M. Bockris, E. Kojonen, J. Amer. Chem. Soc. 82, 4493 (1960)

J. O'M. Bockris and Lowe, J. Sci. Inst. 30, 403 (1953)

A. Borucka, J. O'M. Bockris and J.A. Kitchener, Proc. Roy. Soc. A241, 554 (1957)

A.L. Bowman, Dissertation Abstracts 19, 1926 (1959)

P.C. Carman and L.M. Stein, Trans. Far. Soc. 52, 619 (1956)

H.B.G. Casimir, Rev. Mod. Phys. 17, 343 (1945)

F. Collins and H. Raffel, J. Chem. Phys. 29, 699 (1958)

J.W. Corbett and J.H. Wang, J. Chem. Phys. 25, 422 (1956)

P. Curie, Journal de Physique, 3rd Series, $\underline{3}$, 394 (1894); "Oeuvres de
Pierre Curie" pp.118-141, Gautier-Villon, Paris,(1908)

R.S. Dantuma, Z. Anorg. u. Allgem. Chem. $\underline{175}$, 1 (1928)

Y.K. Delimarskii, Uspekhi Khim. $\underline{23}$, 766 (1954)

Y. K. Delimarskii, B.F. Markov and L.S. Berenblium, Zhurnal. Fiz. Khim.
$\underline{27}$, 1848 (1953)

Y.K. Delimarskii and B.F. Markov, "The Electrochemistry of Fused Salts,"
Sigma Press, Washington D.C., (1961) p. 316

Y.K. Delimarskii, P.P. Turov and E.B. Gitman, Ukrain. Khim. Zhur.
$\underline{21}$, 314 (1955); c.a. $\underline{50}$, 3850g (1956)

S. Djordjevic and G.J. Hills, Trans. Far. Soc. $\underline{56}$, 269 (1960)

P. Drossbach and P. Petrick, Z. Electrochem. $\underline{58}$, 95 (1954)

F.R. Duke and A.L. Bowman, J. Electrochem. Soc. $\underline{106}$, 626 (1959)

F.R. Duke, A.L. Bowman, E. Wolf and H. Garfinkel, Ann. N.Y. Acad. Sci.
$\underline{79}$, 1023 (1960)

F.R. Duke and J.P. Cook, Iowa State Coll. J. of Science $\underline{32}$, 35 (1957)

F.R. Duke and J.P. Cook, Iowa State Coll. J. of Science $\underline{33}$, 81 (1958)
c.a. $\underline{52}$, 17910g (1958)

F.R. Duke and J.P. Cook, J. Phys. Chem. $\underline{62}$, 1593 (1958)

F.R. Duke and R.A. Fleming, J. Electrochem. Soc. $\underline{106}$, 130 (1959);c.a.
$\underline{53}$, 7729g (1959)

F.R. Duke and R. Laity, J. Am. Chem. Soc. $\underline{76}$, 4046 (1954)

F.R. Duke and R. Laity, J. Phys. Chem. $\underline{59}$, 549 (1955)

F.R. Duke and B. Owens, J. Electrochem. Soc., $\underline{105}$, 548 (1958)

F.R. Duke and G. Victor, "Transport Numbers of Some Pure Fused Nitrates
and Nitrites" (in press, 1963)

F.A. Dullien and L.W. Shemilt, Trans. Far. Soc. $\underline{58}$, 244 (1962)

A.S. Dworkin, R.B. Escue and E.R. Van Artsdalen, J. Phys. Chem. $\underline{64}$, 872 (1960)

E. Eastman, J. Am. Chem. Soc. $\underline{48}$, 1482 (1926); $\underline{50}$, 283 (1928)

A. Einstein, Ann. Physik $\underline{19}$, 289 (1906); $\underline{34}$, 591 (1911)

O.A. Esin, J.A. Teterin and I.N. Zakharov, Zhur. Fiz. Khim. $\underline{33}$, 1887 (1959)

H. Eyring and N. Hirai, J. Appl. Phys. $\underline{29}$, 810 (1958)

H. Eyring, T. Ree and N. Hirai, Proc. National Acad. Sciences (U.S.)
$\underline{44}$, 683 (1958)

Fisher and A. Klemm, Z. Naturforsch $\underline{16a}$, 563 (1961)

D.D. Fitts, "Non-Equilibrium Thermodynamics," McGraw-Hill, New York, (1962)

J. Frankel, "Kinetic Theory of Liquids," Oxford, 1946

S. Glasstone, K. Laidler and H. Eyring, "Theory of Rate Processes,"
    Mc Graw-Hill, New York (1941)

H.S. Green in Handbuch der Physik, S. Flugge, ed. (Springer-Berlin,1960),
    Vol. 10, p. 1

G. Hagen, Ann. Phys. Chem. 46, 423 (1839)

G. Harrington and B.R. Sundheim, J. Phys. Chem. 62, 1454 (1958)

E. Helfand, J. Chem. Phys. 33, 319 (1960)

K.F. Herzfeld and T.R. Litovitz, "Absorption and Dispersion of Ultrasonic
    Waves," Academic Press, New York, 1959

R.W. Higgs and T.R. Litovitz, J. Accoust. Soc. Am. 32, 1108 (1960)

J.O. Hirschfelder, C.F. Curtiss and R.B. Bird,"Molecular Theory of
    Gases and Liquids," J. Wiley and Sons, New York, 1954

H. Holtan, Thesis, Utrecht (1953); Tich. Kjem. Bergvesen Met. 12,5(1952)

Huber, Rotter and St. Clair, U.S. Bureau of Mines, Report of Investigator
    1952, 4858, quoted by Bloom and Bockris p. 193

Hunter, J. Amer. Ceram. Soc. 17, 121 (1934)

D. Inman and J. O'M. Bockris, J. Electroanalytical Chem. 3, 126 (1962)

G.J. Janz and J.P.E. McIntyre, Ann. N.Y. Acad. Sci. 79, 761 (1960)

G.J. Janz, C. Solomons and H.J. Gardner, Chem. Rev. 58, 461 (1958)

S. Karpachev and S. Pal'guev, Zhur. fiz. Khim. 23, 942 (1949)

J. Kellner and B.R. Sundheim (in preparation, 1963)

H.H. Kellogg and P. Duby, J. Phys. Chem. 66, 191 (1962)

J.G. Kirkwood, J. Chem. Phys. 14, 180 (1946)

J.G. Kirkwood, R.L. Baldwin, P.J. Dunlop, L.J. Gosting and G. Kegeles,
    J. Chem. Phys. 33, 1505 (1960)

J.G. Kirkwood and B. Crawford, Jr., J. Phys. Chem. 56, 1048 (1952)

. Klemm, Z. Naturforschung 8a, 397 (1953)

. Klemm, Z. Naturforsch. 15a, 173 (1960)

. Klemm, Dis. Far. Soc. 32, 203 (1961)

. Kubo, J. Phys. Soc. Japan 12, 570,1203 (1957)

R.J. Labrie and V.A. Lamb, "Transference Numbers in Pure Molten Sodium Nitrate," Meeting Electrochem. Soc., Detroit, 1961

H.A. Laitinen and W.S. Ferguson, Anal. Chem. 29, 4(1957)

H.A. Laitinen and H.C. Gauer, Anal Chem. Acta 18, 4 (1958)

R. Laity, J. Am. Chem. Soc. 79, 1849 (1957)

R. Laity, J. Chem. Phys. 30, 682 (1959)

R. Laity and F.R. Duke, J. Electrochem. Soc. 105, 97 (1958)

B. Leaf, Phys. Rev. 70, 748 (1946)

O. Lehmann, Wiedem. Annalen d. Phys. 24, p. 24, 145, 147 (1885)

R. Lorenz, die Elektrolyse geschmalzener Salze (in three parts), Halle a.s., Wilhelm Knapp, 1905

R. Lorenz, "Raumerfullung w. Jonen beweglichkeit", Leipzig, 1922 as as quoted by Y.K. Delimarskii and B.F. Markov in "The Electrochemistry of Fused Salts," The Sigma Press, Washington D.C., 1961, p. 316

R. Lorenz and G. Fausti, Z. fur Electrochem. 10, 630 (1904)

R. Lorenz and A. Hochberg, Z. Anorg. u. Allgem. Chem. 94, 317 (1916)

R. Lorenz and G. Janz, J. Phys. Chem. 61, 1683 (1957)

A. Lunden, J. Electrochem. Soc. 109, 260 (1962)

J.D. MacKenzie, Rev. Sci. Inst. 27, 297 (1956)

J.D. MacKenzie in "Physico-Chemical Measurements at High Temperatures", Butterworth, London, 1959, p. 313

J.D. MacKenzie, J. Chem. Phys. 28, 1037 (1958)

V.I. Malkin and B.M. Mogutnov, Izv. Akad. Nauk. SSSR, Otdel Metallurgii y Toplivo 2, 37 (1960)

B.F. Markov, Doklady Akad. Nauk SSSR 108, 115 (1956)

McCallum and Barret, Trans. Brit. Ceram. Soc. 51, 523 (1952)

A.G. Morachewski, J. Applied Chem. of the USSR 33, 1434 (1960)

I.G. Murgulescu and L. Marta, Studii si cercetari de Chimie 3, 1 (1960)

I.G. Murgulescu and D. Topor, Zeit. Phys. Chem (Leipzig) 219, 134 (1962)

I.G. Murgulescu and D. Topor, Zeit. Phys. Chem (Leipzig) (In press)

A.R. Nichols, Jr. and C.T. Langford, J. Electrochem. 107, 842 (1960)

L. Onsager, Phys. Rev. 37, 405 (1931)

L. Onsager, Phys. Rev. 38, 2265 (1931)

G. Perkins, R.B. Escue, J.F. Lamb and J.W. Wimberley, J. Phys. Chem. 64, 1792 (1960)

L. Poincare, Ann. Chem. and Phys. 6, Bd. 21, 338 (1890)

J.L. Poiseuille, Compt. Rend. 11, 961, 104 (1840); ¿2, 112 (1841)

I. Prigogine, Thesis, "Etude Thermodynamique des Processes Irreversibles,"
                    Dunod, Paris and Desoer, Liege (1947)

Rait and Hay, J. Tech. Coll. Glasg. 4, 252 (1938)

S.A. Rice, Phys. Rev. 112, 804 (1958)

S.A. Rice, Trans. Far. Soc. 58, 499 (1962)

S. Rice and Allnatt, J. Chem. Phys. 34, 2144 (1961)

S. Rice and H. Frisch, Ann. Rev. Phys. Chem. 11, 187 (1960)

S. Rice and J. Kirkwood, J. Chem. Phys. 31, 901 (1959)

J.S. Rowlinson and J.R. Townley, Trans. Far. Soc. 49, 1 (1953)

W. Sauerwein and B.R. Sundheim, (in preparation, 1963)

R. Schneebaum, Dissertation, New York University, 1963

R. Schneebaum and B.R. Sundheim, Disc. Far. Soc. 32, 197 (1962)

K.E. Schwartz, Z. Electrochem. 45, 740 (1939)

M.I. Simnad, L. Yang and G. Derge, Trans. AIME 206, 690 (1956)

Spells, Proc. Phys. Soc. (London) 48, 299 (1936)

Spiegler, Trans. Far. Soc. 54, 1408 (1958)

M. Steinberg and N.H. Nachtrieb, J. Am. Chem. Soc. 72, 3558 (1950)

B.R. Sundheim, J. Phys. Chem. 60, 1381 (1956)

B.R. Sundheim, J. Chem. Phys. 27, 791, 1424 (1957)

B.R. Sundheim, J. Phys. Chem. 61, 485 (1957) (a)

B.R. Sundheim, AEC Document No. NYO-7744 (1960)

B.R. Sundheim and J. Rosenstreich, J. Phys. Chem. 63, 419 (1959)

M. Temkin and Khorosin, J. Phys. Chem. URSS 26, 500 (1952)

C. Thalmayer, J. Bruckenstein and D.M. Gruen (in press)

J. W. Tomlinson in "Physico-chemical Measurements at High Temperatures,"
                    J.O'M. Bockris, J. White, J. MacKenzie eds.,
                    Academic Press, 1959

L.E. tTopol and R. A. Osteryoung, J. Phys. Chem 66, 1587 (1962)

H. Towers and J. Chipman, Trans. AIME 209, 769 (1957)

H. Towers, Paris and J. Chipman, Trans. AIME 197, 1455 (1953)

H.J.V. Tyrrll, "Diffusion and Heat Flow in Liquids," Butterworth's,
                    London, 1961

E.R. Van Artsdalen, D. Brown, A.S. Dworkin and F.J. Miller, J. Am. Chem.
Soc. 78, 1772 (1956)

E.R. Van Artsdalen and I.S. Jaffe, J. Phys. Chem. 59, 118 (1955);
60, 1125 (1956)

L.E. Wallin, Z. Naturforsch. 17a, 191 (1962); 17a, 195 (1962)

H. Winterhager and L. Werner, Forschung Wirvshaft und Verkeherministerium,
Nordheim-Wesfalen 34, (1956); 38, (1957); data
given by Bockris and Crook p. 127 and by E.W. Yim
and M. Feinlieb, J. Electrochem. Soc. 104, 626 (1957)

L.E. Wallin and A. Lunden, Z. Naturforsch. 14a, 262 (1959)

Warburg, Wiedem Ann. d. Phys. 21, 622 (1884)

E.W. Washburn, J. Am. Chem. Soc. 31, 322 (1909)

E.D. Wolf, Iowa State University of Sci. and Technology, Thesis #61-
3053, (1961)

J.M. Wood, Meeting Electrochem. Soc., Washington,D.C., May, 1957

L. Yang, C.Y. Chien and G. Derge, unpublished report

L. Yang and Simnad in "Physico-chemical Measurements at High Temperatures,"
Academic Press, New York, 1959, p. 295

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